Novel Routes for Sintering of Ultra-high Temperature Ceramics and their Properties

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14. ABSTRACT
The project has been focused on phase equilibria research, development of phase diagrams of the ternary systems ZrO_2-CeO_2-Ln_2O_3(Ln=La_2O_3,Eu_2O_3,Gd_2O_3) and some of boundary binary systems, as well as manufacturing and characterization of dense, optically transparent ceramics based on $LaYO_3$and $Y_3Al_5O_{12}$ phases. First developed phase diagrams of the ternary systems ZrO_2-CeO_2-Ln_2O_3 (Ln = La, Eu, Gd) and binary systems ZrO_2-Gd_2O_3, CeO_2-Gd_2O_3, CeO_2-Eu_2O_3have been presented as a collection of isothermal and polythermal sections in the temperature range from 600 to 1500 ^{o}C. The solubility of components, extension of one, two and three phase fields and mechanisms of phase reactions have been determined. Lattice parameters for solid solutions were calculated. The results have been summarized along the rows of the systems ZrO_2-Ln_2O_3, CeO_2-$Ln_2O_3$and ZrO_2-CeO_2-Ln_2O_3.The pyrochlore-type or defect fluorite-type phases of the formulae $Zr(Ce)_2Gd_2O_7$when doped with scintillator Eu^{2+}represent a subject of interest for future ceramic laser matrices. The nanosize powders of doped Nd(Yb):$LaYO_3$ and Nd:$Y_3Al_5O_{12}$ phases containing various amount of dopants have been chemically prepared. Particle size distribution was narrow in the particle size range of 10-22 nm. Coarsening of particles to 300 nm and faceting of particles were carried out to allow manipulation in strong magnetic field using EPD or SC techniques. The neodymia doped garnet samples showed residual porosity less than 0.2% with good transparency of 70-72% after RCS.Neodymiadopant led to instability of the $LaYO_3$ phase. The rear earth ions such as Er^{3+} and Yb^{3+}may be used as laser dopants. The Yb:$LaYO_3$ ceramics textured under strong magnetic field has shown density of 99.0-99.2. The samples were found semi-transparent (average transparency is less than 45%), but more transparent along c-axis.

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FINAL REPORT
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Project title: "Phase equilibria in advanced ternary oxide systems and study of optically transparent ceramic nanomaterials"

Reporting period: November 1, 2011 – October 31, 2014

Frantsevich Institute for Problems in Materials Science NAS of Ukraine

Project Manager: Prof. Elena Andrievskaya

Main goal of the project:

The proposal is aimed at study of phase equilibria, development of phase diagrams of the ternary systems ZrO_2-CeO_2-Ln_2O_3(La_2O_3,Eu_2O_3,Gd_2O_3), as well as manufacturing and studying optically transparent ceramics based on lanthana-yttria perovskite ($LaYO_3$) yttria-alumina garnet ($Y_3Al_5O_{12}$). The sub-targets are: Study of phase equilibria and development of phase diagrams in the ternary systems ZrO_2—CeO_2—Ln_2O_3(La_2O_3, Eu_2O_3, Gd_2O_3), to determine temperature intervals of phase stability, concentration dependences of lattice parameters, solubility of components, especially luminescent-active ions; synthesis of nanosize powders for various solid solutions based on $LaYO_3$ and $Y_3Al_5O_{12}$ in the particle size range 10-15 nm, valid for manufacturing dense nanocrystalline ceramics; study of rate controlled sintering of these powders until 99.9% of theoretical density controlling both pore-and-grain size evolution under gas atmosphere with definite oxygen partial pressure; study of optical properties for ceramics.

1. Phase equilibria in the ZrO_2—CeO_2—Ln_2O_3(La_2O_3, Eu_2O_3, Gd_2O_3) systems

The phase equilibria research in the ternary ZrO_2-CeO_2-Ln_2O_3 systems represents basic knowledge and practical interests. The systems including zirconia, ceria, europia, dysprosia and ytterbia are of practical interest to create novel alternative oxide materials of structural and functional applications with advanced characteristics [1-16, 24-27].

For instance, doped zirconia, ceria and lanthanide oxides are widely used for thermal barrier coatings, ionic conductors in solid oxide fuel cells, catalysts etc. [17-23, 27]. Substantial potential these systems demonstrate in the nuclear energy engineering for both nuclear fuel and inert matrices to safely store nuclear wastes [26]. At present the search of ceramics matrix immobilizing plutonium is a hot topic for these materials. The inert matrix material should meet the following requirements: high cross section of neutron catching, good enough thermal stability, low thermal conductivity and low thermal expansion coefficient, lack of phase transitions. The high temperature structural ceramics with low thermal expansion is valuable in neutron reactor components. To immobilize the transuranic elements, the ceramic matrix appears to be the best choice because of high thermodynamic stability for a long life time of exploration.

The lattice of the pyrochlore-type phase ($A_2B_2O_7$), containing Zr^{4+} ions as the main cation of the compound $M_2Zr_2O_7$ (M = three and/or four charged cation) is reliable and substantiated matrix for concentrated nuclear wastes. The ordered pyrochlore phase $Eu_2Zr_2O_7$ is also perspective thermal isolator [3, 15, 24]. These properties of REO zirconates are attractive for thermal barrier coatings in gas turbines [15, 22]. Chemical composition corresponding to europium zirconate ($Eu_2Zr_2O_7$) exists as a disordered phase of fluorite type (disordered cations and vacancies) at high temperatures, meanwhile at low temperatures the ordering results in pyrochlore-type phase (where cations and vacancies are ordered). The pyrochlore type phase $Eu_2Zr_2O_7$ transforms to the defect fluorite by

ordering/disordering mechanism at relatively high temperature ~ 2100 °C. Because of similarity of physic-chemical properties of plutonia and ceria, CeO_2 is often used as a surrogate material instead of PuO_2.

Materials based on ceria, zirconia doped with REO are perspective for bio-medical applications, energy conversion and machine-building, optical systems and catalysts because of uniqueness of its properties. Phase diagrams of the given systems are considered physicochemical background for such materials like solid electrolytes in fuel cells, catalyst's carriers, refractory ceramics, barrier coatings etc. Solid solutions based on ceria represent the most prospective electrolyte materials operating at moderate temperatures, because their ionic conductivity and sensitivity to oxygen partial pressure is much higher than that for yttria stabilized ZrO_2 (YSZ). Thermal barrier coatings with double ceramic layer: CeO_2 and 8YSZ, 8YSZ and $Ln_2Zr_2O_7$- the pyrochlore type phase - demonstrate high melting temperature, lack of phase transitions at room and elevated operation temperatures, low thermal conductivity, chemical inertness, thermal expansion corresponding to that of metal substrate, good adhesion to substrate and low sintering rate, porous microstructure. Additions of low-valence dopants, such as Ln^{3+} and Y^{3+}, solid solutions of the system CeO_2–ZrO_2 allow suppression of undesirable segregation of ions in the phase based on ceria zirconia in so called ceramic carriers of catalysts, which sustainably operate at moderate temperatures for a long time [8-12].

Methodology

In accordance with the plan, the samples for phase equilibria in the ternary ZrO_2-CeO_2-Ln_2O_3 system and binary CeO_2-Ln_2O_3, ZrO_2-Ln_2O_3 systems in the full range of concentrations. As input components the zirconyl-nitrate $ZrO(NO_3)_2$ and cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ of "pure" grade, nitric acid "pure for analysis", La_2O_3, Eu_2O_3 and Gd_2O_3 with content of the main component not less than 99.99 %.

Samples were prepared with the concentration step of 1-5 mol. % from nitrate solutions followed by evaporation and thermal decomposition of nitrates until oxides followed by firing at 1200 °C for 2 hours. The powders were pressed into tablets of 5 mm in diameter and 4 mm in height under pressure of 10 MPa. For studying the systems ZrO_2-CeO_2-Ln_2O_3 the samples of the compositions along the sections: ZrO_2 - (50 mol. % CeO_2 - 50 mol. % Ln_2O_3), ZrO_2 - (90 mol. % CeO_2 - 10 mol. % Ln_2O_3), ZrO_2 - (10 mol. % CeO_2 - 90 mol. % Ln_2O_3), CeO_2 - (69 mol. % ZrO_2 – 31 mol. % Ln_2O_3) and some iso-concentrates were taken for consideration.

Accordingly to the plan, the annealing of samples for the phase diagram research in the ternary ZrO_2-CeO_2-Ln_2O_3 system has been carried out at 1100 °C and in the binary CeO_2-Ln_2O_3, ZrO_2-Ln_2O_3 systems at 1100 and 1500 °C.

Phase equilibria in the systems ZrO_2-CeO_2-Ln_2O_3, were studied at 1100 °C using thermal treatment in the H23U5T furnace in air. The samples were heated from room temperature to given one with the rate of 3.5 degr/min. The annealing regime is non-stop. The periodical control of the homogenization completeness was provided. Then samples were grinded again pressed and placed into furnace for annealing. The period was not less than 150 hours. Cooling down was quite slow. Total duration of this unique experiment in the ZrO_2-CeO_2-Ln_2O_3 systems and boundary binary systems at **1100 °C** was about **13000 hours**.

To study the phase equilibria in the ZrO_2-Gd_2O_3 system at melting temperatures, the samples with concentration step of 1-10 mol. % were prepared by traditional ceramic method, mechanical mixing of input oxides. The powders were mixed in agate mortar. Powders were consolidated into discs of 20 mm in diameter and of 15 mm in height using steel mold under pressure of 10 MPa. Melting was carried out in the optical furnace. Crystallization in the radial - symmetrical temperature field optical furnace have own specific features. The heat source in the optical furnace is concentrated luminous flux. The power density flux of light energy in the focal zone has Gauss distribution. When placing the material in the focal zone the relatively flat shallow melt pool is

formed. Its size gradually increases, until energy losses such as heat conductivity through the pool bottom, light irradiation from the pool surface would become equal to falling energy. After reaching equilibrium, the size of bath is stabilized. With decreasing power density of the falling energy flow, the process of crystallization has begun. The melt crystallizes in the direction from the boundary to the center of the melt pool in the center. The last drop of melt solidifies in the center of the focal zone. The shape of received ingot surface depends on the ratio of the density of the melt and the solid phase properties at crystallization temperature.

Due to features of bulk alloys melting, samples for phase equilibria study were prepared by the method of sequential deposition of layers in the focal zone optical furnace. Thus there is a consistent increase of ingot thickness and texture formation under high (several hundred degrees per millimeter), recurrent temperature gradients in the direction from the bottom surface of the melt pool to its upper surface. The samples melted, cooled followed by annealed at 1500 °C were studied by XRD, petrography and electron microscopy methods. Phase composition of the samples has been determined with the aid of XRD and LRSA methods. The XRD used the powder method of sampling at troom temperature ($Cu_{K\alpha}$ irradiation). The recording scanning rate was 1-4 degr/min in the diapason of 2θ angles from 15 to 80°. The periods of crystalline lattices were calculated by the less square method of using LATTIC code with an accuracy bellow 0.0004 nm for cubic phase.

The crystal-optic characteristics of the phases obtained were determined under polarized microscope "MIH-8". The refraction indexes were measured in immersion liquids (solution of arsenic tribromide in methylene iodide or alloys of sulfur with selenium) with accuracy ±0.02.

Microstructures were studied on polished surfaces of the samples annealed and melted using local x-ray spectral analysis, on the microscope SUPERPROBE-733 (JEOL, Japan, Palo Alto, CA) in both back scattered electrons (BEI) and secondary electrons (SEI). The composition of the sample has been controlled with the aid of spectral and chemical analysis.

1.1. Phase equilibria in the ZrO_2—CeO_2—La_2O_3 systems

Isothermal section of the phase diagram of the ZrO_2-CeO_2-La_2O_3 system at 1100 °C

The phase diagram of the ZrO_2-CeO_2-La_2O_3 system at high temperatures has been previously studied in our recent work. Present research is focused on phase equilibria in this system at low temperatures, in particular, at 1100 °C. The isothermal section of the ternary phase diagram of the system ZrO_2-CeO_2-La_2O_3 at 1100 °C has been developed and presented here in Fig. 1.1. The chemical and phase composition of the samples annealed at 1100 °C, lattice parameters for the equilibrium phases at given temperature are presented in the Fig. 1.2.

In the ZrO_2-CeO_2-La_2O_3 system at 1100 °C there had been find five fields of solid solutions based on monoclinic (M) and tetragonal (T) ZrO_2, hexagonal (A) La_2O_3, cubic form of fluorite type (F) CeO_2 and an ordered phase of pyrochlore type $La_2Zr_2O_7$ (Py). New phases were not found in this system. To determine boundaries of the phase fields the concentration dependence of lattice parameters for elementary cells of the phases (Fig. 1.2). These results were confirmed by microscopy and XRD data (Figs 1.3-1.7 and Tables 1.1, 1.2).

Using parameters of elementary cells of the pyrochlore phase in the three-phase samples, as well as XRD data in combination with SEM gave coordinates for configurative points of the tie-line triangles (Py+T+F), (Py+T+M) i (Py+F+A) (Table. 1.1). In the field with high concentration of ZrO_2 the solid solutions based on monoclinic and tetragonal ZrO_2 were found. No substantial solubility of CeO_2 and La_2O_3 in the M-ZrO_2 was determined. The boundary of the homogeneity field of the solid solution based on M-ZrO_2 at 1100 °C passes close to the composition of 99 mol % ZrO_2-0.5 mol % CeO_2-0.5 mol % La_2O_3. The narrow field of the solid solutions based on T-ZrO_2 is prolated along the boundary binary system ZrO_2-CeO_2 (2-18 mol % CeO_2). The solubility of La_2O_3 in T-ZrO_2 is not high achieving ~ 1 mol %, confirmed by XRD.
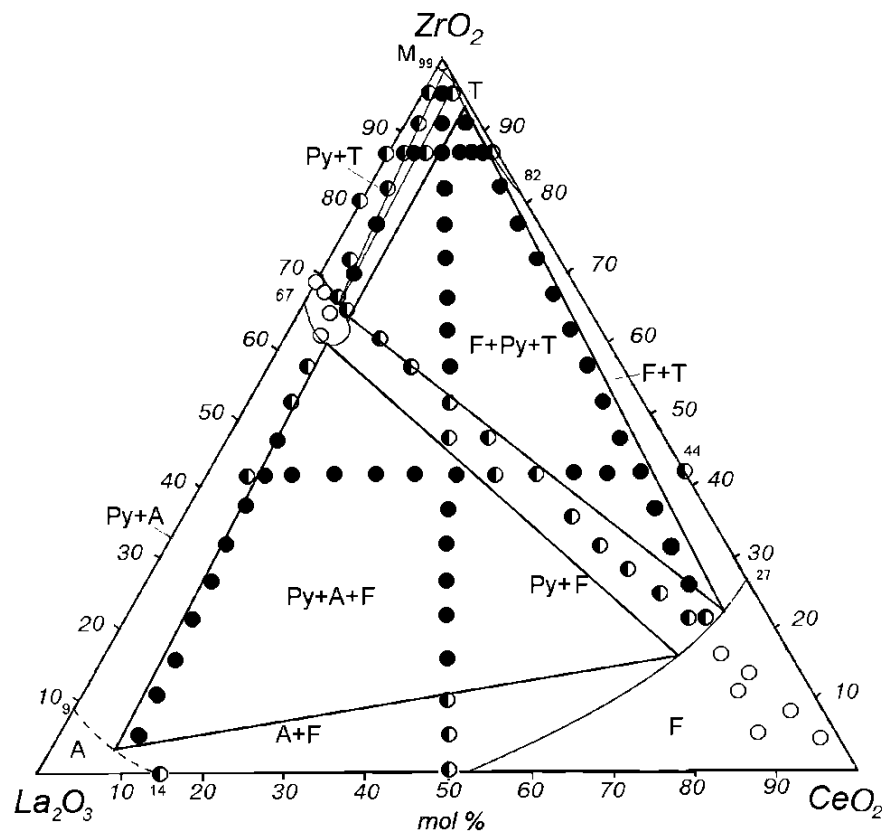
Fig. 1.1 - Isothermal cross section of the ternary diagram of the ZrO_2-CeO_2-La_2O_3 system at temperature 1100 °C (○ − one-phase, ◐ - two-phase, ● − three-phase).
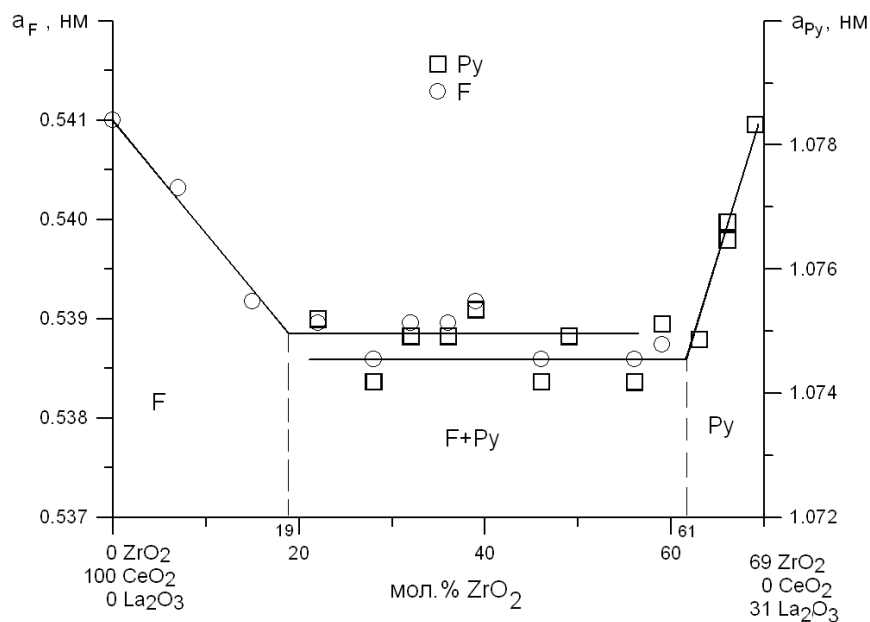

Fig. 1.2 - Concentration dependences of the lattice parameters of the solid solutions F (○) and Py (□) by the cross section CeO_2 - (69 mol. % ZrO_2 - 31 mol. % La_2O_3) in the system ZrO_2-CeO_2-La_2O_3 after annealing at 1100 °C.

Table 1.1 Coordinates of the tie-line triangle in the ZrO$_2$-CeO$_2$-La$_2$O$_3$ system corresponding to three-phase equilibrium in this system at 1100 °C

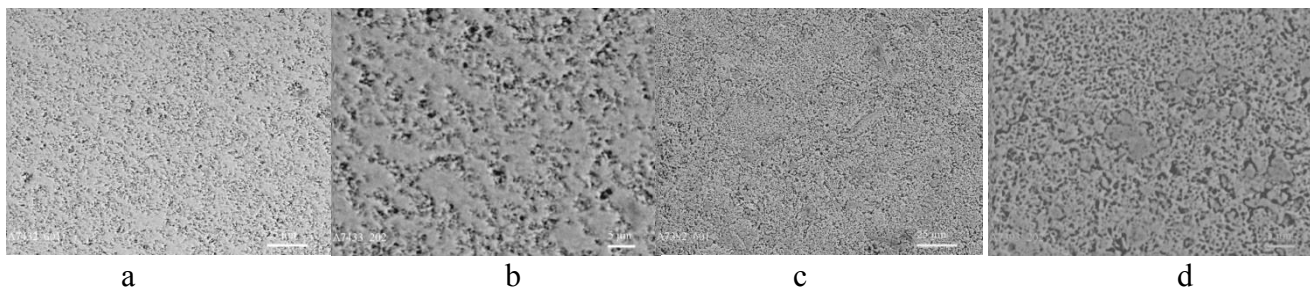| Phase field	Coordinates of the tie-line triangle, mol %									
	M		T		Py		F		A	
	ZrO$_2$	CeO$_2$	ZrO$_2$	CeO$_2$	ZrO$_2$	CeO$_2$	ZrO$_2$	CeO$_2$	ZrO$_2$	CeO$_2$
Py+T+M	99.0	0.5	96.5	3.0	66.0	4.0	-	-	-	-
F+Py+T	-	-	93.0	6.0	64.0	7.0	24.0	73.0	-	-
Py+A+F	-	-	-	-	60.0	6.0	16.0	70.0	3.0	8.0

a   b   c   d

Fig 1.3-Microstructure of the F phase in the system ZrO$_2$-CeO$_2$-La$_2$O$_3$ after annealing at 1100 °C:
a) 3 mol%ZrO$_2$ – 95% mol CeO$_2$ – 2mol % La$_2$O$_3$, <F>, BEI, × 600;
b) 3 mol%ZrO$_2$ – 95% mol CeO$_2$ – 2mol % La$_2$O$_3$, <F>, BEI, × 2000;
c) 11 mol %ZrO$_2$ – 80.5 mol % CeO$_2$ – 8.5mol % La$_2$O$_3$, <F>, BEI, × 600;
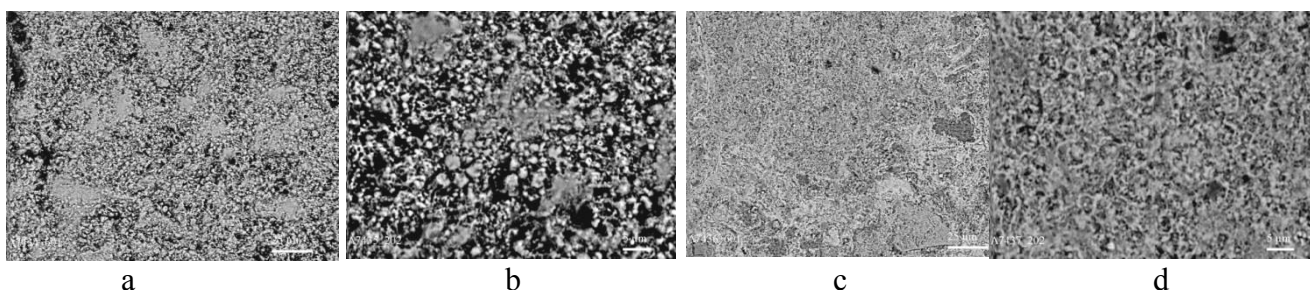d) 11 mol %ZrO$_2$ – 80.5 mol % CeO$_2$ – 8.5mol % La$_2$O$_3$, <F>, BEI, × 2000;

a   b   c   d

Fig 1.4-Microstructure of the three phase samples (Py+F+A*) of the system ZrO$_2$-CeO$_2$-La$_2$O$_3$ annealed at 1100 °C:
a) 42 mol% ZrO$_2$ - 24 mol% CeO$_2$ - 34 mol% La$_2$O$_3$, tr, BEI, ×600;
b) 42 mol% ZrO$_2$ - 24 mol% CeO$_2$ - 34 mol% La$_2$O$_3$, Py+F+A* tr., BEI, , ×2000;
c) 42 mol% ZrO$_2$ - 30 mol% CeO$_2$ - 28 mol% La$_2$O$_3$, Py+F+A* tr., BEI, ×600;
d) 42 mol% ZrO$_2$ - 30 mol% CeO$_2$ - 28 mol% La$_2$O$_3$, Py+F+A* tr., BEI, ×2000;
light grains – <F-CeO$_2$>, gray – <A-La$_2$O$_3$>, dark – La$_2$Zr$_2$O$_7$, black – pores.

a   b   c   d
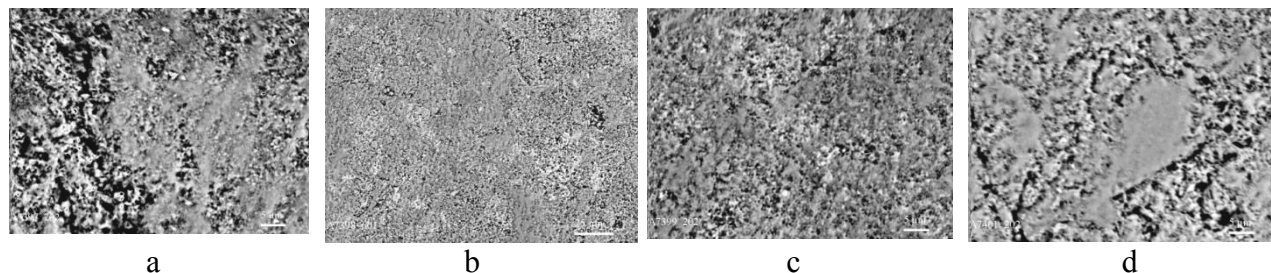
Fig. 1.5-Microstructure of the samples in the system ZrO$_2$-CeO$_2$-La$_2$O$_3$ after annealing at 1100 °C:
a) 82 mol% ZrO$_2$ -1 mol% CeO$_2$ -17 mol% La$_2$O$_3$, Py+M↑, BEI, ×2000;
c) 91 mol% ZrO$_2$-1 mol% CeO$_2$-8 mol% La$_2$O$_3$, Py+M, BEI, ×600;
d) 91 mol% ZrO$_2$-1 mol% CeO$_2$-8 mol% La$_2$O$_3$, Py+M, BEI, ×2000;
gray grains - La$_2$Zr$_2$O$_7$, dark grains - <M-ZrO$_2$>, black – pores.
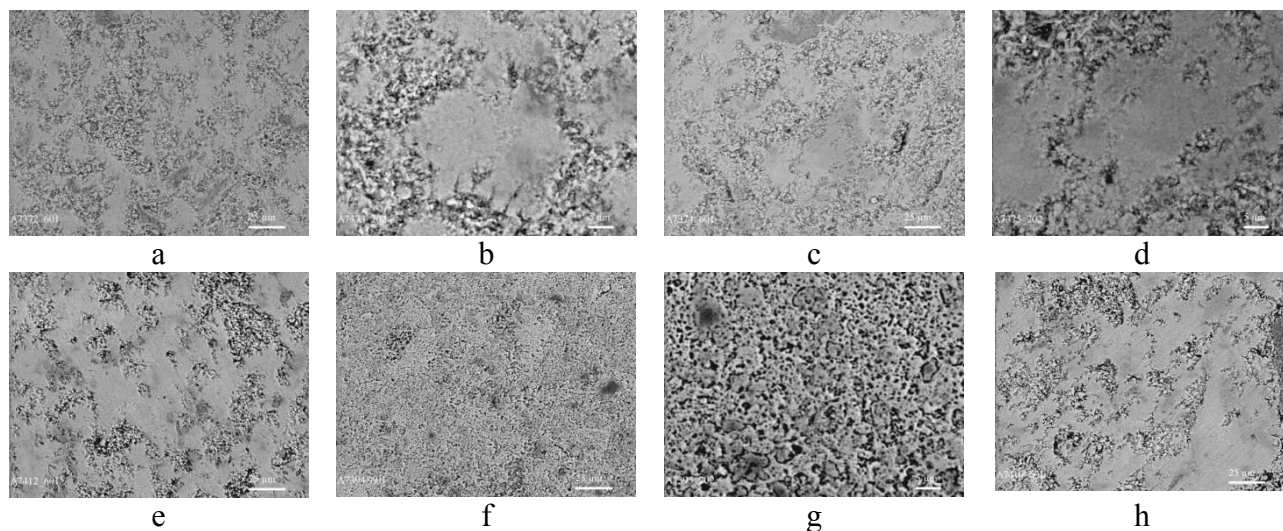
Fig 1.6-Microstructures of the samples of the system ZrO_2-CeO_2-La_2O_3 after annealing at 1100 °C:
a) 47 mol% ZrO_2 - 26.5 mol% CeO_2 - 26.5 mol% La_2O_3, F+Py, BEI, ×600;
b) 47 mol% ZrO_2 - 26.5 mol% CeO_2 - 26.5 mol% La_2O_3, F+Py, BEI, ×2000;
c) 52 mol% ZrO_2 - 24 mol% CeO_2 - 24 mol% La_2O_3, F+Py, BEI, × 600;
d) 52 mol% ZrO_2 - 24 mol% CeO_2 - 24 mol% La_2O_3, F+Py, BEI, × 2000;
e) 16 mol% ZrO_2 - 76 mol% CeO_2 - 8 mol% La_2O_3, F-CeO_2+Py tr., BEI, ×600;
f) 16 mol% ZrO_2 - 76 mol% CeO_2 - 8 mol% La_2O_3, F-CeO_2+Py tr., BEI, ×2000;
g) 59 mol% ZrO_2 - 14 mol% CeO_2 - 27 mol% La_2O_3, BEI, Py+F tr., × 600;
h) 59 mol% ZrO_2 - 14 mol% CeO_2 - 27 mol% La_2O_3, Py+F tr., BEI, × 2000;
light grains – <F-CeO_2>, dark grains – $La_2Zr_2O_7$., black – pores.
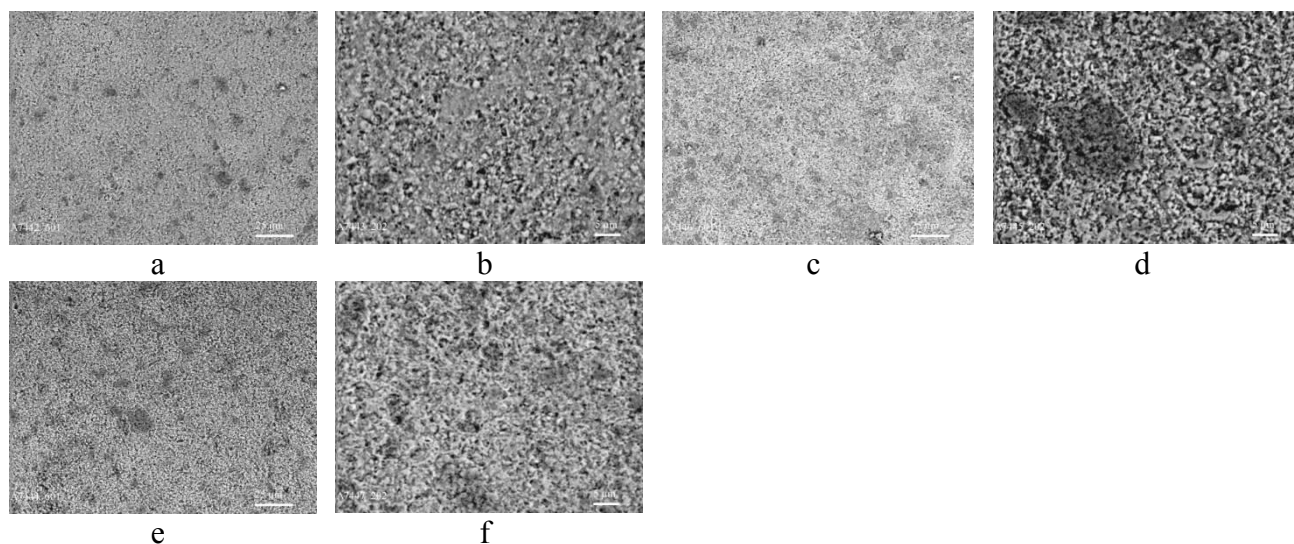

Fig. 1.7-Microstructures of the samples in the system ZrO_2-CeO_2-La_2O_3 after annealing at 1100 °C:
a) 42 mol% ZrO_2 - 44 mol% CeO_2 – 14 mol% La_2O_3, Py+F+T* tr, BEI, × 600;
b) 42 mol% ZrO_2 - 44 mol% CeO_2-14 mol% La_2O_3, Py+F+T* tr, BEI, × 2000;
c) 42 mol% ZrO_2 - 48 mol% CeO_2 - 10 mol% La_2O_3, Py+F+T**tr, BEI, ×600;
d) 42 mol% ZrO_2 - 48 mol% CeO_2 - 10 mol% La_2O_3, Py+F+T**tr, BEI, ×2000;
e) 42 mol% ZrO_2 - 54 mol% CeO_2 - 4 mol% La_2O_3, F+T**tr↑+Py tr↓, BEI, ×600;
f) 42 mol% ZrO_2 - 54 mol% CeO_2 - 4 mol% La_2O_3, F+T**tr↑+Py tr↓, BEI, ×2000;
light grains – <F-CeO_2>, gray – $La_2Zr_2O_7$, dark – <T-ZrO_2>tr, black – pores.

Table 1.2 Phase composition and lattice parameters of the phases in the ZrO_2-CeO_2-La_2O_3 system after annealing at 1100 °C for 12780 hours. (XRD data)

Chemical composition, mol %			Phase composition and lattice parameters of elementary cells, a (nm) by XRD data
ZrO_2	CeO_2	La_2O_3	
1	2	3	4
Перерiз ZrO_2 - (50 mol % CeO_2 - 50 mol % La_2O_3)			
32	34	34	<F>basis (0.5152) + Py (1.0829) + <A>tr
37	31.5	31.5	<F>↓ + Py basis. (1.0820) + <A>tr
47	26.5	26.5	Py (1.0785) +<F>tr (0.5393)
52	24	24	Py basis (1.0760) + <F>tr↓ (0.5380)
57	21.5	21.5	Py basis (1.0749) + <F>tr (0.5366) + <T>**tr
62	19	19	Py (1.0738) +<F>tr↓ (0.5356) +<T>**tr
72	14	14	Py (1.0749)+<F>tr + <T>**↑
77	11.5	11.5	Py (1.0752)+<F>tr (0.5324) + <T>**
82	9	9	Py (1.0737)+<F> (0.5245) + <T>**↑
87	6.5	6.5	Py (1.0752) + <T>**+<F>tr↓ (0.5238)
91	4.5	4.5	Py↓ (1.0752) + <T>*↑ + <F>tr↓↓ (0.5230)
96	2	2	<M>basis+ <T>* + Py↓ (1.0765)
Section ZrO_2 - (90 mol % CeO_2 – 10 mol % La_2O_3)			
0	90	10	<F> (0.5443)
5.4	85	9.6	<F>
11	80.5	8.5	<F> (0.5423)
16	76	8	<F> (0.5397)
21	71	8	<F> (0.5369) + Py tr (1.0738)
26	67	7	<F>basis (0.5357) + Py (1.0714)
32	62	6	<F>basis (0.5349) + Py tr (1.0702) + <T>**tr
37	57	6	<F>basis (0.5341)+Py tr (1.0699) +<T>*tr
47	47	6	<F>basis (0.5341) +Py tr (1.0699) +<T>*tr
52	43	5	<F>basis (0.5341) + <T>** + Py tr↓↓
57	39	4	<F>basis (0.5346) + <T>*↑ + Py tr (1.0693)
62	34	4	<F> (0.5341) + <T>** + Py (1.0682)
67	30	3	<F> (0.5342) + <T>** + Py (1.0683)
72	25	3	<F> (0.5333) + <T>*↑ + Py (1.0665)
76	21	3	<T>*↑ + <F> (0.5351) + Py (1.0701)
81	17	2	<T>* + <F>↓ (0.5350) + Py (1.0699)
91	8	1	<T>*basis +<F>↓ (0.5341) +Py↑ (1.0682)
96	3	1	<T>*+Py tr↓ (1.0760)
100	0	0	<M>
Section ZrO_2 - (10 mol % CeO_2 - 90 mol % La_2O_3)			
62	3	35	Py (1.0794)
67	2	31	Py (1.0761) + <M>tr
72	2	26	Py (1.0752) + <M> tr↑
77	2	21	Py (1.0772) + <M>↑ + <T>**tr
82	1	17	Py (1.0772) + <M>↑
86	1	13	Py + <M>
91	1	8	Py + <M>
95.7	0.3	4	Py↓ (1.0763) + <M>↑

Section CeO$_2$- (69 mol % ZrO$_2$-31 mol % La$_2$O$_3$)

69	0	31	Py (1.078338)
68	1	31	Py
66	3	31	Py (1.076476)
66	4	30	Py basis (1.0768) + <T>*tr
63	9	28	Py (1.0749) + <F>tr
59	14	27	Py (1.0751) + <F>tr (0.5389)
56	19	25	Py (1.0742) + <F>↑ (0.5392)
49	29	22	Py (1.0749) + <F>↑
46	34	20	Py (1.0742) +<F> (0.5386)
39	44	17	Py↓ (1.0754) + <F> (0.5392)
36	49	15	Py↓ (1.0749) + <F> (0.53896)
32	54	14	Py↓ (1.0749) + <F> (0.53896)
28	59	13	Py tr↓ (1.0742) + <F>↑ (0.5391)
22	69	9	Py tr↓↓ (1.0752) + <F>↑ (0.53896)
15	79	6	<F> (0.5392)
7	90	3	<F> (0.5403)
3	95	2	<F>
0	100	0	<F> (0.5409)

Iso-concentration line 42 mol % ZrO$_2$

42	24	34	Py (1.0886)+<F>(0.5437)+<A>*tr (a=0.6557; c=0.3835)
42	30	28	Py↓ (1.0831)+<F>(0.5414)+<A>*tr (a=0.6568; c=0.3828)
42	35	23	Py↓ (1.0785) + <F> (0.5396)
42	40	18	Py (1.0785) + <F> (0.5391)
42	44	14	<F> (0.5374) + Py (1.0749) + <T>*tr
42	48	10	<F> (0.5368) + Py (1.0737) + <T>**tr
42	54	4	<F> (0.5358) + <T>**tr↑ + Py tr↓ (1.0716)
42	58	0	<F>basis (0.5367) + <T>**

Iso-concentration line 86 mol % ZrO$_2$

86	0	14	<M>+Py
86	1	13	<M> + Py (1.0772)
86	2	12	<M> + Py (1.0772)
86	3	11	<M> + Py (1.0766)
86	5	9	<T>**↑ + Py (1.0763)
86	9	5	<T>**↑ + Py↓ (1.0752) + <F>tr↑
86	11	3	<T>** + Py↓ (1.0725)+ <F>↑
86	12	2	<T>** + <F>↑ + Py↓ (1.0714)
86	13	1	<T>** + <F>
86	14	0	<T>*

* Under given conditions (T=1100 °C, 12780 hours., in air) the tetragonal phase T-ZrO$_2$ and hexagonal phase A-La$_2$O$_3$ cannot be stabilized on quenching. Instead of them the monoclinic phase M-ZrO$_2$ and hexagonal phase La(OH)$_3$ have been determined instead;

** the partial stabilization of the T- and A- phases has been established.

Legend: <A> – solid solutions based on hexagonal La$_2$O$_3$; <T> – solid solutions based on tetragonal modification of ZrO$_2$; <M> – solid solutions based on monoclinic HfO$_2$; <F> – solid solutions based on cubic modifications of the fluorite-type CeO$_2$; Py – ordered phase La$_2$Zr$_2$O$_7$ of the pyrochlore type. Other notations: basis – the main phase, tr – traces of a phase, ↑ – phase amount increases, ↓ – amount decreases.

The boundary of the homogeneity field of the solid solution based on T-ZrO_2 at 1100 °C passes near the compositions: 96 mol % ZrO_2-3 mol % CeO_2-1 mol % La_2O_3 – two-phase (T+Py tr), 91 mol % ZrO_2-8 mol % CeO_2-1 mol % La_2O_3 – three-phase (T basis+F+Py), 86 mol % ZrO_2-13 mol % CeO_2-1 mol % La_2O_3 – two-phase (T+F). Note, solid solutions based on T-form of ZrO_2 at 1100 °C, similarly to those obtained at 1500 °C cannot be stabilize on cooling or even on quenching. On XRD patterns, obtained at room temperatures we found the traces of the M-ZrO_2 lines. Partial stabilization of the T-phase in several composition has been revealed (Table 1.2). Microstructure studies allow findings of phase transitions, such as polysynthetic twinning.

Solid solution based on lanthanum zirconate at 1100 °C co-exists in equilibrium with all phases, existing in the system ZrO_2-CeO_2-La_2O_3, and forms solid solutions of substitution type in the binary systems. The maximum solubility of ceria (to 8 mol % CeO_2) in $La_2Zr_2O_7$ is observed on the cross-section of CeO_2 – (69 mol % ZrO_2 – 31 mol % La_2O_3), similarly to the sections at 1500, 1450, 1250 °C. The boundary of the homogeneity field of the $La_2Zr_2O_7$ phase in equilibrium with T-ZrO_2 and A-La_2O_3 at 1100 °C demonstrates substantial extension along the binary system ZrO_2-La_2O_3.

The isothermal cross-section in the sub-section of the ZrO_2-$La_2Zr_2O_7$-CeO_2 system at 1100 ° C is characterized by two three-phase fields (Py+F+T) and (Py+T+M). The boundaries of the three-phase fields are determined by samples located along the iso-concentration line 86 mol % ZrO_2. The microstructures of the samples, characterizing three-phase field (Py+F+T) in the zirconia-rich sub-system, are presented in Fig. 1.7 a-f. In the samples, containing 42 mol % ZrO_2-44 mol % CeO_2-14 mol % La_2O_3, 42 mol % ZrO_2-48 mol % CeO_2-10 mol % La_2O_3, 42 mol % ZrO_2-54 mol % CeO_2-4 mol % La_2O_3, three phases are clearly detected: gray – anisotropic (T), light – isotropic (F) with inclusions of dark-gray phase (Py). The results of x-ray microspectral analysis confirm three phase co-existence.

The maximal extension demonstrates the homogeneity field of the solid solution based on F-CeO_2. The boundary of the F-phase is curved to the CeO_2 corner and passes along the boundary binary systems ZrO_2-CeO_2 (73-100 mol % CeO_2) and CeO_2-La_2O_3 (50-100 mol % CeO_2). The specific microstructures of the F-phase are presented in Fig. 1.3 a-d.

Extension of the F-phase is determined by x-ray diffraction patterns of the following samples: 16 mol % ZrO_2-76 mol % CeO_2-8 mol % - one-phase (F), 21 mol % ZrO_2-71 mol % CeO_2-8 mol % La_2O_3, La_2O_3 22 mol % ZrO_2-69 mol % CeO_2-9 mol % La_2O_3 – two-phase (F+Py). The boundary solubility of the F-phase along the section CeO_2 - (69 mol % ZrO_2 – 31 mol % La_2O_3) achieves 19 mol % ZrO_2-72 mol % CeO_2-9 mol % La_2O_3. The lattice parameters in this raw changes from a=0.5409 nm for pure CeO_2 to a=0.5389 nm for two-phase samples, which includes 22 mol % ZrO_2-69 mol % CeO_2-9 mol % La_2O_3 (Fig. 1.5).

The fluorite-type phase exists in two-phase (A+F), (T+F), (Py+F) and three-phase (Py+F+T), (Py+A+F) fields. The isothermal section of the partial sub-system La_2O_3-$La_2Zr_2O_7$-CeO_2 at 1100 °C crosses one three-phase (Py+A+F) and three two-phase (Py+F, Py+A, A+F) fields. The specific microstructures corresponding to two-phase field on phase diagram (Py+F), shown in Fig. 1.6 a-j. In the samples containing 47 mol % ZrO_2-26.5 mol % CeO_2-26.5 mol % La_2O_3, 52 mol % ZrO_2-24 mol % CeO_2-24 mol % La_2O_3, 16 mol % ZrO_2-76 mol % CeO_2-8 mol % La_2O_3, 59 mol % ZrO_2-14 mol % CeO_2-27 mol % La_2O_3, 56 mol % ZrO_2-14 mol % CeO_2-27 mol % La_2O_3, 49 mol % ZrO_2-29 mol % CeO_2-22 mol % La_2O_3, two structural components differ by contrast: light-gray isotropic phase — F with inclusions of other dark isotropic phase — Py. In the sub-system with low mount of ZrO_2, the homogeneity fields of the solid solutions based on F-CeO_2, A-La_2O_3 and phase Py dominate.

Thus, in the present research we first time studied phase equilibria in the systems of ZrO_2-CeO_2-La_2O_3 and CeO_2-La_2O_3 in the whole interval of concentrations and at temperatrues 1450, 1250, 1100 °C. The elements of the phase diagram have been developed for the binary system CeO_2-La_2O_3 and isothermal sections of the ternary ZrO_2-CeO_2-La_2O_3 system at given temperatures.

Formation of the finite-solubility solid solutions based on input components was revealed in the binary and ternary diagrams. Phase equilibria in the system at temperatures 1500, 1450, 1250 and 1100 °C look similar, however, substantial differences are observed, which are defined by constitution of the boundary binary system and features of the phase formation in the ternary system. In opposite to constitution of isothermal section at 1450, 1250 °C the section of the ZrO_2-CeO_2-La_2O_3 system at 1100 °C consists of (Py+T+F, Py+F+A, Py+T+M) three phase fields and six two-phase fields (Py+A, Py+T, Py+F, Py+M, F+T, A+F). From the given isothermal sections at various temperatures, the extension of the homogeneity and two-phase fields shortens, and the extension of the three-phase fields gradually widens, number of the phase fields increases due to tetragonal – monoclinic transformation in zirconia.

The diagram of the system ZrO_2-CeO_2-La_2O_3 at 1100 °C has been studied in details in the zirconia-rich field, but the lanthana-rich part of the diagram requires more efforts to be completely studied.

1.2. Phase equilibria in the ZrO_2—CeO_2—Eu_2O_3 system

The system ZrO_2-CeO_2-Eu_2O_3 is one of the most interesting and prospective ternary system. Development of new generation materials requires phase equilibria research, phase relationships and stability in this system at various temperatures.

Phase relations in the boundary binary systems ZrO_2-CeO_2, ZrO_2-Eu_2O_3 were studied incompletely [24], and phase equilibria data about the CeO_2-Eu_2O_3 system is contradictory [25-35].

Zirconia reaction with ceria has been studied in [36-79]. The diagram of the ZrO_2-CeO_2 system has been developed in [11, 36-38] (Fig. 1.8). Several discrepancies, however, were found in the phase diagrams proposed as at temperatures bellow 1100 °C with uncertain coordinates for tetragonal to monoclinic eutectoid and $Ce_2Zr_3O_{10}$ (Φ) phase, as above 1600 °C because of partial transformation of CeO_2 to Ce_2O_3.

In the low-temperature area ($\leq$ 1500 °C), the state diagrams of the ZrO_2-CeO_2 system includes the following phases: monoclinic M-ZrO_2 in the range from 0 to 1 mol % CeO_2 at 1100 °C, tetragonal T-ZrO_2 in the range from 0 to 18 mol % CeO_2 at 1500, 1450 °C and from 2 to 18 mol % CeO_2 at 1100 °C and cubic phase of the fluorite type structure F-CeO_2 in the interval from 56 to 100 mol % CeO_2 at 1500 °C, from 60 to 100 mol % CeO_2 at 1450 °C and from 73 to 100 mol % CeO_2 at 1100 °C. The wide two-phase field (F+T) has been revealed in the concentration range from 18 to 56 mol % CeO_2 at 1500 °C, from 18 to 60 mol % CeO_2 at 1450 °C and two heterogenic fields at 1100 °C: wide two-phase fields (F+T) in the concentration range from 18 to 73 mol % CeO_2 and narrow two-phase field (M+T) in the concentration range from 1 to 2 mol % CeO_2. The tetragonal modification of ZrO_2 cannot be quenched, the monoclinic phase M-ZrO_2 was always indicated instead [36-39].

The system ZrO_2-Eu_2O_3 has been studied using various methods for sample manufacturing, techniques for phase composition research and their properties' studies [63, 80-98]. This phase diagram was studied most completely in [24, 96, 97]. The reaction of zirconia with europia was studied in details in the wide temperature range of 1250-2700 °C, and the full diagram was studied for the system ZrO_2-Eu_2O_3 (Fig. 1.9).
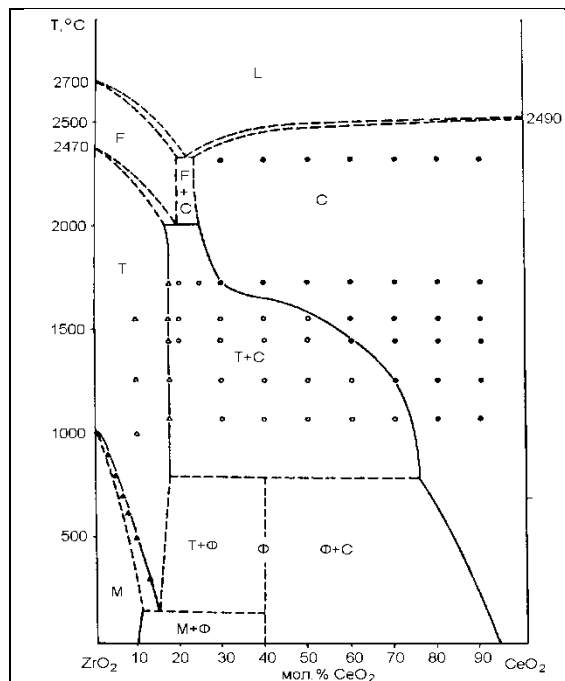
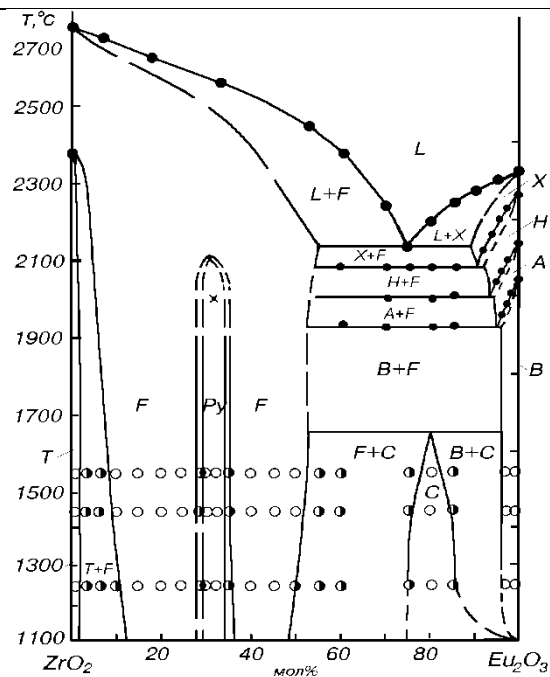| Fig. 1.8 – Phase diagrams of the binary system ZrO₂-CeO₂ [38]	Fig. 1.9 – Phase diagram of the binary system ZrO₂-Eu₂O₃ (●- thermal analysis in air using solar energy; ○- one-phase, ◐ - two-phase samples) [24]

The liquidus surface of the ZrO_2-Eu_2O_3 system is characterized by eutectic reaction $L \rightleftarrows F + X$ (2130 °C, 26 mol % ZrO_2). Additives of europium oxide to zirconia decrease melt temperatures and phase transition points in ZrO_2. Dissolution of 1 mol% Eu_2O_3 in ZrO_2 is enough to stabilize cubic solid solution of fluorite type at 1250 °C. of Eu_2O_3 in T-ZrO_2 is about ~ 1 mol % Eu_2O_3 (1250 °C) becomes wider to 2 mol % at higher temperature of 1550 °C.

The two phase field (T + F) shrinks with temperature decrease: from 1÷13 mol% Eu_2O_3 at 1250 °C to 2÷8 mol% Eu_2O_3 at 1550 °C. Existence of intermediate phase $Eu_2Zr_2O_7$ with pyrochlore-type structure and lattice period a = 1.0540 ± 0.0005 nm (in the composition 66.7 mol% ZrO_2 at 1550 °C) and refraction index 2.07 < n < 2.10. The homogeneity field of the pyrochlore phase at 1250 and 1550 °C is located in the range 30÷35 mol% Eu_2O_3 and 30÷34 mol % Eu_2O_3, respectively. The solubility gap splits the field of the fluorite type solid solutions in the considered here temperature and concentration range, which is from 1250 to 1550 °C and 13÷25 and 37÷45, 8÷28 and 36÷52 mol% Eu_2O_3, respectively. Lattice parameters (a) increase from 0.5159 to 0.5225 nm and from 0.5286 to 0.5335 nm at 1550 °C. The refraction index of the isotropic F-phase n = 2.07 (for composition 45 mol% Eu_2O_3, 1550 °C). There are two-phase (F + Py) fields separating the homogeneity fields of one pyrochlore field and two fluorite field.

In the europia-rich phase field, the phase relations are complicated much by polymorphism of Eu_2O_3. Dissolving of zirconia in europia leads to stabilization of cubic europia and increases its temperature range of existence. When temperature increased, the size of homogeneity field of C-Eu_2O_3 phase decreases from 25÷15 mol% ZrO_2 (1250 °C) to 21÷19 mol % ZrO_2 (1550 °C), and boundaries of two-phase fields (F + C) and (B + C) widen from 55÷25 and 15÷2 mol% ZrO_2 (1250 °C) to 48÷21 and 19÷4 mol% ZrO_2 (1550 °C), respectively.

Solid solutions based on tetragonal (T) and cubic of fluorite structure (F) ZrO_2, cubic form (C, X), monoclinic (B), hexagonal (A, H) modifications of Eu_2O_3, and ordered intermediate phase $Eu_2Zr_2O_7$ of pyrochlore type (Py), as well as two-phase fields T+F, F+Py, B+C, F+C, F+(B, A, H, X) were found and studied.

Boundaries of the homogeneity field for the B-type Eu_2O_3 solid solutions are not wider than 2 mol % ZrO_2 (1250) i 4 mol % ZrO_2 (1550 °C). Boundary solubility of ZrO_2 in polymorphs B-, A-

, H- i X- Eu_2O_3 achieves 6, 7, 8 and 10 mol% ZrO_2. Temperatures of eutectoid transformations have been determined as 1920, 2000, 2080 $\pm$ 20 °C.

In the system ZrO_2-Eu_2O_3, the following phases were found at 1500 °C: B-Eu_2O_3 in the interval from 0 to 3 mol% ZrO_2, C-Eu_2O_3 in the range from 17 to 20 mol% ZrO_2, F-ZrO_2 in the interval from 45 to 63 mol% ZrO_2 and from 72 to 90 mol% ZrO_2, $Eu_2Zr_2O_7$ in the interval from 65 to 70 mol% ZrO_2, T-ZrO_2 in the interval from 98 to 100 mol% ZrO_2. The two-phase fields were determined: (B + C) in the range 3 to 17 mol% ZrO_2, (C + F) in the range 20-45 mol% ZrO_2, (F + Py) - from 63 to 65 mol% ZrO_2 and from 70 to 72 mol% ZrO_2 and (F + T) in the concentration range 90÷98 mol % ZrO_2.

The system CeO_2-Eu_2O_3 has been studied incompletely. No phase diagrams were published yet. There is very limited information about some phases and their properties [25-35]. With the aid of XRD analysis at room temperature the reaction between CeO_2 and Eu_2O_3 has been studied [28, 35]. Samples have been prepared at 1200 °C by solid phase sintering in air of pure oxides obtained by nitrate decomposition at 500 °C. Two types of solid solutions with cubic structures (CaF_2-type and Tl_2O_3-type) inherent in pure oxides [35] exist in this system. Phase reactions in the system CeO_2-Eu_2O_3 were studied in [26, 29-33]. It was shown that the cubic solid solutions of the fluorite type (F-CeO_2) are formed at temperature 1400 °C in the range from pure CeO_2 to 40 mol% Eu_2O_3 and from 40 to 100 mol% Eu_2O_3 (C-Eu_2O_3). Lattice parameters of cubic solid solutions vary from a = 5.411 nm for pure CeO_2 to a = 5.441 nm in composition, which contains 40 mol% Eu_2O_3 and (45 mol% Eu_2O_3) to a = 10.868 nm (100 mol% Eu_2O_3). Existence of two-phase field in the given system has not been found [26]. The thermal expansion coefficient $\alpha_a \cdot 10^6$ (0-1400°C) of solid solutions $Ce_{1-x}Eu_xO_{2-x/2}$ increases 9.89; 11.44; 11.6; 13.17 in the raw x = 0.90; 0.55; 0.45; 0.1, respectively [26].
Some characteristics formed in the given system are shown in the Table. 1.3-1.5.

Table 1.3 – Dielectric constants (ε_∞) of materials $Ce_{0.8}Ln_{0.2}O_{2-\delta}$ (Ln = Gd, Eu) [31]

Composition	ε_∞ 300 ºC	ε_∞ 400 ºC	ε_∞ 500 ºC	ε_∞ 550 ºC
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	5,44	12,29	16,74	20,05
$Ce_{0.8}Eu_{0.2}O_{2-\delta}$	6,09	7,91	13,12	19,64

Table 1.4 – Conductivity and its activation energy for the solid solutions $Ce_{0.8}Ln_{0.2}O_{2-\delta}$ (Ln = Gd, Eu) by the data [33]

Composition	E_a, (eV) (480-550 ºC)	σ_{gi} (Sm/sm) at 550 ºC	σ_{gb} (Sm/sm) at 550 ºC	σ (Sm/sm) при 550 ºC
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	1,07	$5,8 \cdot 10^{-4}$	$7,3 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$
$Ce_{0.8}Eu_{0.2}O_{2-\delta}$	0,91	$3,45 \cdot 10^{-4}$	$4,4 \cdot 10^{-4}$	$1,39 \cdot 10^{-4}$

Table 1.5 – Thermal expansion coefficient for pure CeO_2 and one doped with Ln^{3+} [34]

Composition	Thermal expansion coefficient $\alpha_a \cdot 10^6$ (0-1200 °C)
CeO_2	12.68
$Ce_{0.5}La_{0.5}O_{1.75}$	10.48
$Ce_{0.5}Nd_{0.5}O_{1.75}$	11.87
$Ce_{0.5}Sm_{0.5}O_{1.75}$	12.10
$Ce_{0.5}Eu_{0.5}O_{1.75}$	12.61
$Ce_{0.5}Gd_{0.5}O_{1.75}$	12.47
$Ce_{0.5}Dy_{0.5}O_{1.75}$	11.77
$Ce_{0.5}Ho_{0.5}O_{1.75}$	11.95
$Ce_{0.5}Er_{0.5}O_{1.75}$	12.29
$Ce_{0.5}Yb_{0.5}O_{1.75}$	12.32
$Ce_{0.5}Lu_{0.5}O_{1.75}$	12.45

First, phase equilibria in the ternary ZrO_2-CeO_2-Eu_2O_3 system at temperature 1500 °C and binary CeO_2-Eu_2O_3 system at temperatures 1500, 1100 and 600 °C have been studied in the whole interval of concentrations. The following samples have been prepared along the six sections: ZrO_2 - (50 mol % CeO_2 - 50 mol % Eu_2O_3), ZrO_2 - (10 mol % CeO_2 - 90 mol % Eu_2O_3), ZrO_2 - (30 mol % CeO_2 - 70 mol % Eu_2O_3), ZrO_2 - (70 mol % CeO_2 - 30 mol % Eu_2O_3), CeO_2 - (67 mol % ZrO_2 – 33 mol % Eu_2O_3), Eu_2O_3 - (60 mol % ZrO_2 - 40 mol % CeO_2) and iso-concentration lines: 20 mol % ZrO_2, 45 mol % ZrO_2 and 85 mol % ZrO_2.

Thermal treatment of samples of the ternary ZrO_2-CeO_2-Eu_2O_3 system at 1500 °C was carried out in two stages: in the furnace with heating elements H23U5T at 1100 °C for 452 h and in the furnace with $MoSi_2$ heating elements at 1500 °C for 150 h in air.

Annealing of samples of the binary CeO_2-Eu_2O_3 system was carried out at 1500 °C (for 170 h), 1100 °C (16800 h), 600 °C (33061 h). Similarly, to study phase equilibria in the CeO_2-Eu_2O_3 system at 1500 °C firing of samples was carried out in two stages: in the furnace with heating elements H23U5T at 1100 °C for 17 h and in the furnace with $MoSi_2$ heating elements at 1500 °C for 170 h in air.

The system CeO_2-Eu_2O_3

Solid state reactions of CeO_2 (fluorite type, F) and Eu_2O_3 (monoclinic, B) has shown, that in the system CeO_2-Eu_2O_3 at temperature 1500 °C three solid solutions formed: two cubic F-CeO_2 and C-Eu_2O_3, and one monoclinic B-Eu_2O_3, corresponding to pure components (Fig. 1.10). Temperature decrease to 600 °C results in decrease of the phase fields number. The monoclinic phase B - Eu_2O_3 is not stable bellow 1000 °C [25].

The chemical and phase compositions of the samples, annealed at 1500, 1100 and 600 °C, lattice parameters of equilibrium phases, are listed in the Tables 1.6-1.8. The boundaries of the homogeneity fields for solid solutions based on F-CeO_2, C-Eu_2O_3 and B-Eu_2O_3 at 1500 °C are determined by compositions 20-25 mol% Eu_2O_3, 80-85 mol% Eu_2O_3 and 0.5-99 mol % Eu_2O_3 (Table 1.6). At 1100 °C the boundaries of homogeneity fields for the phases F-CeO_2 and C-Eu_2O_3 are determined by compositions 20÷25 mol% Eu_2O_3 and 90÷99 mol% Eu_2O_3, respectively (Table 1.7). When temperature decreasing to 600 °C, the homogeneity fields of the solid solutions based on F-CeO_2 and C-Eu_2O_3 becomes gradually narrower. The boundaries of them at 600 °C are determined by configuration points of 10÷15 mol% Eu_2O_3 and 97÷98 mol% Eu_2O_3, respectively (Table 1.8). Variation of lattice parameter against chemical composition (concentration of Eu_2O_3) of the F-CeO_2 solid solution is shown in Fig. 1.11.

From these data we have concluded, that the solubility of Eu_2O_3 in the F- CeO_2 solid solution achieves 20 mol % at 1500, 1100 °C and 10 mol% at 600 °C. The lattice parameter increases from a=0.5409 nm in pure CeO_2 to a=0.5425 nm in boundary solid solution (1500, 1100 °C) and a=0.5422 nm (600 °C) for the sample containing 15 mol% Eu_2O_3. The XRD and petrography research coincide with electron microscopy observations and measurements. Typical microstructures of the phases formed in the CeO_2-Eu_2O_3 system at temperatures 1500, 1100, 600 °C are shown in Figs. 1.12-1.13. The microstructures of two phase samples (B + C) annealed at 1500 °C are presented in Fig. 1.12 a-d. In the samples containing 4 mol% CeO_2-96 mol% Eu_2O_3 and 5 mol% CeO_2-95 mol% Eu_2O_3 two structural components were found as different by contrast (Fig. 1.12 a). The light phase is a matrix of the monoclinic B europia by the data of microdifraction analysis.

Another phase looks like dark inclusions can be identified as cubic (C) modification of Eu_2O_3, which has been confirmed by the XRD analysis (Table. 1.6) and petrography. The absolutely dark, opaque and anisotropic grains of monoclinic B phase have been observed on reflection, which is a matrix filled with randomly distributed small-to-medium inclusions of light,

isotropic, transparent C-Eu$_2$O$_3$ phase. When the ceria content increasing the amount of isotropic transparent C-phase growing.

Table 1.6 - Chemical and phase composition, parameters of elementary cells of the system CeO$_2$-Eu$_2$O$_3$ after annealing at 1500 °C for 170 hours. (XRD data, petrography and electron microscopy)

Chemical composition, mol. %		Phase composition	Parameters of elementary cells, nm ($a \pm 0.0002$)					
CeO$_2$	Eu$_2$O$_3$		<F>	<C>	<B>			
			a	a	a	b	c	β
1	2	3	4	5	6	7	8	9
0	100	<B>	-	-	1.4328	0.3579	0.8636	92.30
1	99	<B> basis + <C>	-	1.0854	1.6388	0.3626	0.8644	97.11
2	98	<B> basis + <C>↑	-	1.0841	1.4146	0.3596	0.8711	87.80
3	97	<B> basis + <C>↑	-	1.0839	1.4404	0.3573	0.8892	89.36
4	96	<B> basis + <C>	-	1.0841	1.5552	0.3596	0.8667	93.88
5	95	<B> + <C>	-	1.0837	1.5601	0.3668	0.8727	101.2
10	90	<C> basis↑ + <B>	-	1.0855	1.7250	0.3647	0.8810	99.60
15	85	<C> + <B> tr	-	1.0844	-	-	-	-
20	80	<C>	-	1.0856	-	-	-	-
25	75	<C>	-	1.0863	-	-	-	-
30	70	<C> basis + <F> tr	-	1.0853	-	-	-	-
35	65	<C> basis + <F> tr	-	1.0863	-	-	-	-
40	60	<C> basis + <F> tr	-	1.0856	-	-	-	-
45	55	<C> basis + <F>↑	0.5423	1.0863	-	-	-	-
50	50	<C> basis + <F>↑	0.5423	1.0860	-	-	-	-
55	45	<C> + <F>↑	0.5423	1.0845	-	-	-	-
60	40	<C>↓ + <F>↑	0.5425	1.0867	-	-	-	
65	35	<F> basis + <C>↓	0.5410	1.0820	-	-	-	
70	30	<F> basis + <C> tr↓	0.5424	1.0847	-	-	-	-
75	25	<F> + <C> tr	0.5423	-	-	-	-	-
80	20	<F> basis	0.5425	-	-	-	-	-
85	15	<F>	0.5423		-	-	-	-
90	10	<F>	0.5418		-	-	-	-
95	5	<F>	0.5413		-	-	-	-
0	100	<F>	0.5409		-	-	-	-

Phase identificator: <B> – soid solution based on monoclinic Eu$_2$O$_3$; <C> – solid solutions based on cubic modification of Eu$_2$O$_3$; <F> – solid solutions of cubic phase with fluorite-type of CeO$_2$. Other conditions: basis – phase dominating in the compositions, tr – phase traces, ↑ – increasing, ↓ – decrease.
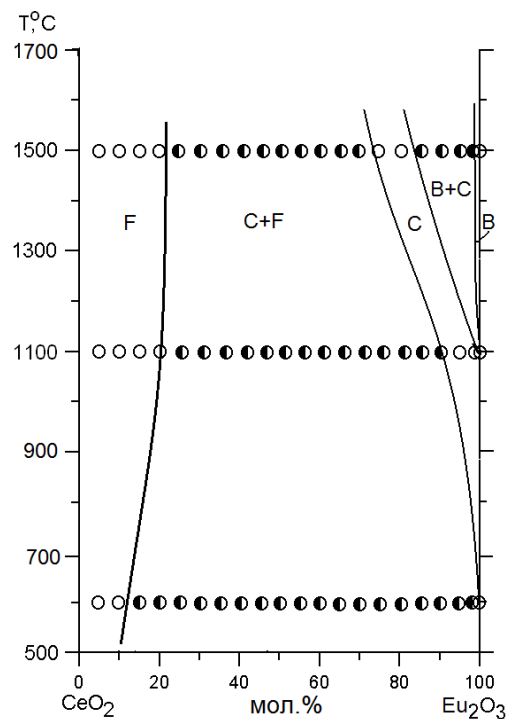
Table 1.7 - Chemical and phase composition, parameters of elementary cells of the system CeO_2-Eu_2O_3 after annealing at 1100 °C for 15960 hours. (XRD data, petrography and electron microscopy)

Chemical composition, mol. %		Phase composition and lattice parameters byXRD data, nm	Parameters of elementary cells, nm $(a \pm 0.0002)$	
CeO_2	Eu_2O_3		\<F\>	\<C\>
			a	a
1	2	3	4	5
0	100	\<B-Eu_2O_3\> ($a = 1.4882$, $b = 0.3562$, $c = 0.8960$, $\gamma = 90.2562$)	-	-
1	99	\<C-Eu_2O_3\> basis + \<B-Eu_2O_3\> tr.	-	1.0840
2	98	\<C-Eu_2O_3\>	-	1.0844
3	97	\<C-Eu_2O_3\>	-	1.0843
4	96	\<C-Eu_2O_3\>	-	1.0838
5	95	\<C-Eu_2O_3\>	-	1.0843
10	90	\<C-Eu_2O_3\> basis + \<F-CeO_2\> tr.	-	1.0846
15	85	\<C-Eu_2O_3\> basis + \<F-CeO_2\> tr.	-	1.0843
20	80	\<C-Eu_2O_3\> + \<F-CeO_2\> tr.	-	1.0842
25	75	\<C-Eu_2O_3\> basis + \<F-CeO_2\> ↑	-	1.0847
30	70	\<C-Eu_2O_3\> basis + \<F-CeO_2\>↑	-	1.0840
35	65	\<C-Eu_2O_3\> + \<F-CeO_2\>	-	1.0845
40	60	\<C-Eu_2O_3\> + \<F-CeO_2\>	0.5431	1.0857
45	55	\<C-Eu_2O_3\> basis + \<F-CeO_2\>↑	0.5431	1.0857
50	50	\<C-Eu_2O_3\>↓ + \<F-CeO_2\>	0.5430	1.0868
55	45	\<C-Eu_2O_3\>↓ + \<F-CeO_2\>↑	0.5431	1.0861
60	40	\<C-Eu_2O_3\>↓ + \<F-CeO_2\>↑	0.5424	1.0864
65	35	\<F-CeO_2\>↑ + \<C-Eu_2O_3\>↓↓	0.5434	1.0867
70	30	\<F-CeO_2\> basis + \<C-Eu_2O_3\>↓↓	0.5425	1.0861
75	25	\<F-CeO_2\> + \<C-Eu_2O_3\> tr.	0.5427	-
80	20	\<F-CeO_2\> basis	0.5425	-
85	15	\<F-CeO_2\>	0.5422	
90	10	\<F-CeO_2\>	0.5420	
95	5	\<F-CeO_2\>	0.5412	
0	100	\<F-CeO_2\>	0.5409	

Table 1.8 - Chemical and phase composition, parameters of elementary cells of the system CeO_2-Eu_2O_3 after annealing at 600 °C for 33061 hours. (XRD data, petrography and electron microscopy)

Chemical composition, mol. %		Phase composition	Parameters of elementary cells, nm ($a \pm 0.0002$)	
			\<F\>	\<C\>
CeO_2	Eu_2O_3		a	a
1	2	3	4	5
0	100	\<C-Eu₂O₃\>	-	1.0837
1	99	\<C-Eu₂O₃\>	-	1.0838
2	98	\<C-Eu₂O₃\>	-	1.0821
3	97	\<C-Eu₂O₃\> basis + \<F-CeO₂\> tr	-	1.0846
4	96	\<C-Eu₂O₃\> + \<F-CeO₂\> tr	-	1.0847
5	95	\<C-Eu₂O₃\> basis + \<F-CeO₂\> tr незнач.	-	1.0840
10	90	\<C-Eu₂O₃\> + \<F-CeO₂\> tr	-	1.0840
15	85	\<C-Eu₂O₃\> basis + \<F-CeO₂\> tr	0.5420	1.0840
20	80	\<C-Eu₂O₃\> + \<F-CeO₂\> tr ↑	0.5422	1.0844
25	75	\<C-Eu₂O₃\> basis + \<F-CeO₂\> tr	-	1.0833
30	70	\<C-Eu₂O₃\> basis + \<F-CeO₂\>	0.5420	1.0840
35	65	\<C-Eu₂O₃\> + \<F-CeO₂\>	0.5416	1.0828
40	60	\<C-Eu₂O₃\> ↓ + \<F-CeO₂\> ↑	0.5416	1.0842
45	55	\<C-Eu₂O₃\> basis + \<F-CeO₂\>	0.5414	1.0840
50	50	\<C-Eu₂O₃\>↓ + \<F-CeO₂\>	0.5416	1.0829
55	45	\<C-Eu₂O₃\>↓ + \<F-CeO₂\>↑	0.5410	1.0821
60	40	\<C-Eu₂O₃\>↓ + \<F-CeO₂\>↑	0.5414	1.0829
65	35	\<F-CeO₂\>↑ + \<C-Eu₂O₃\>↓↓	0.5415	1.0827
70	30	\<F-CeO₂\> +\<C-Eu₂O₃\>	0.5416	1.0832
75	25	\<F-CeO₂\> basis +\<C-Eu₂O₃\> tr	0.5411	1.0821
80	20	\<F-CeO₂\> basis + \<C-Eu₂O₃\> tr↓↓	0.5414	1.0828
85	15	\<F-CeO₂\> basis + \<C-Eu₂O₃\> tr↓↓↓	0.5422	1.0820
90	10	\<F-CeO₂\> basis	0.5410	-
95	5	\<F-CeO₂\>	0.5410	-
0	100	\<F-CeO₂\>	0.5409	-

Phase identificator: \<B\> – soid solution based on monoclinic Eu_2O_3; \<C\> – solid solutions based on cubic modification of Eu_2O_3; \<F\> – solid solutions of cubic phase with fluorite-type of CeO_2. Other conditions: basis – phase dominating in the compositions, tr – phase traces, ↑ – increasing, ↓ – decrease.

(○ – one-phase, ◐ - two-phase samples)

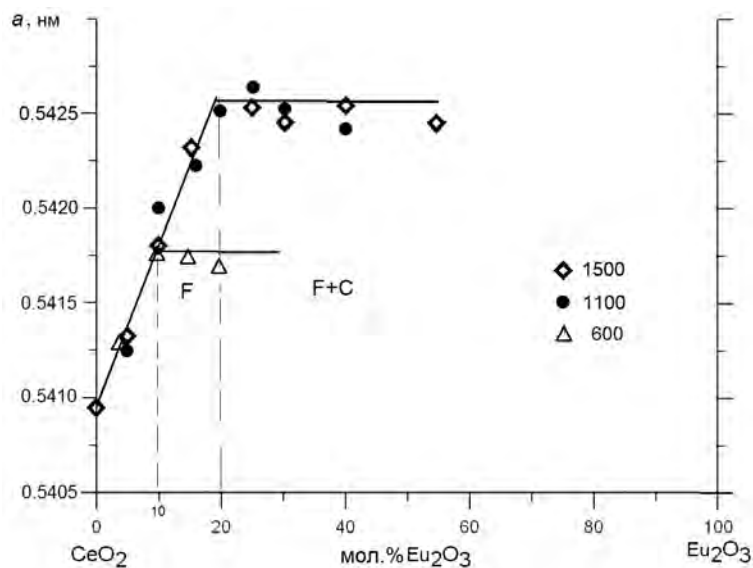Fig. 1.10 – Phase diagram in the system CeO_2-Eu_2O_3 at 600-1500 °C

Fig. 1.11 – Concentration dependence of elementary lattice parameters of the solid solutions based on F-CeO_2 in the system CeO_2-Eu_2O_3 after annealing at (◇) 1500 °C, (●) 1100 °C and (△) 600 °C

The grain size of solid solutions of fluorite type F-CeO_2 grows from 41 to 81 nm. These data are presented in Table 1.9.

Table 1.9 – Particle size of the solid solution F-CeO_2 in the system CeO_2-Eu_2O_3 in the temperature interval 600-1500 °C

Composition of the solid solution	Particle size, nm		
	1500 °C	1100 °C	600 °C
$Ce_{0.95}Eu_{0.05}O_{1.95}$	54	65	81
$Ce_{0.9}Eu_{0.1}O_{1.925}$	44	65	81
$Ce_{0.85}Eu_{0.15}O_{1.9}$	41	54	54

In the samples containing from 10 to 15 mol% CeO_2, the cubic modification of europia becomes basis (Fig. 1.12 d). In the Fig. 1.12 d the fractography clearly shows fragile type of fracture in the microstructure of C-Eu_2O_3 including multiple pores. Fine grain structure of the one phase field (C-Eu_2O_3) is presented in Fig. 1.12 e-f. Further increasing of ceria content in the sample, results in rude relief on the polished surface and sharp edges (Fig. 1.12 f). The traces of cubic phase with fluorite-type cerium oxide appear in the sample containing 30 mol% CeO_2-70 mol% Eu_2O_3. By the data of back scattered electron microscopy (BEI), two phases were revealed (C-Eu_2O_3 + F-CeO_2), different by morphology and surface contrast. The oriented light gray stripes related to the solid solutions (C-Eu_2O_3) and fine grain dark grains of near spherical shape (F-CeO_2) (Fig. 1.12 g, h). By the data of petrography in the reflected light, the main part of microstructure includes isotropic dark phase of europia with light isotropic inclusions of F-CeO_2. It's worth paying attention, that the color of the phase under electron microscope and petrography microscope are strongly different.
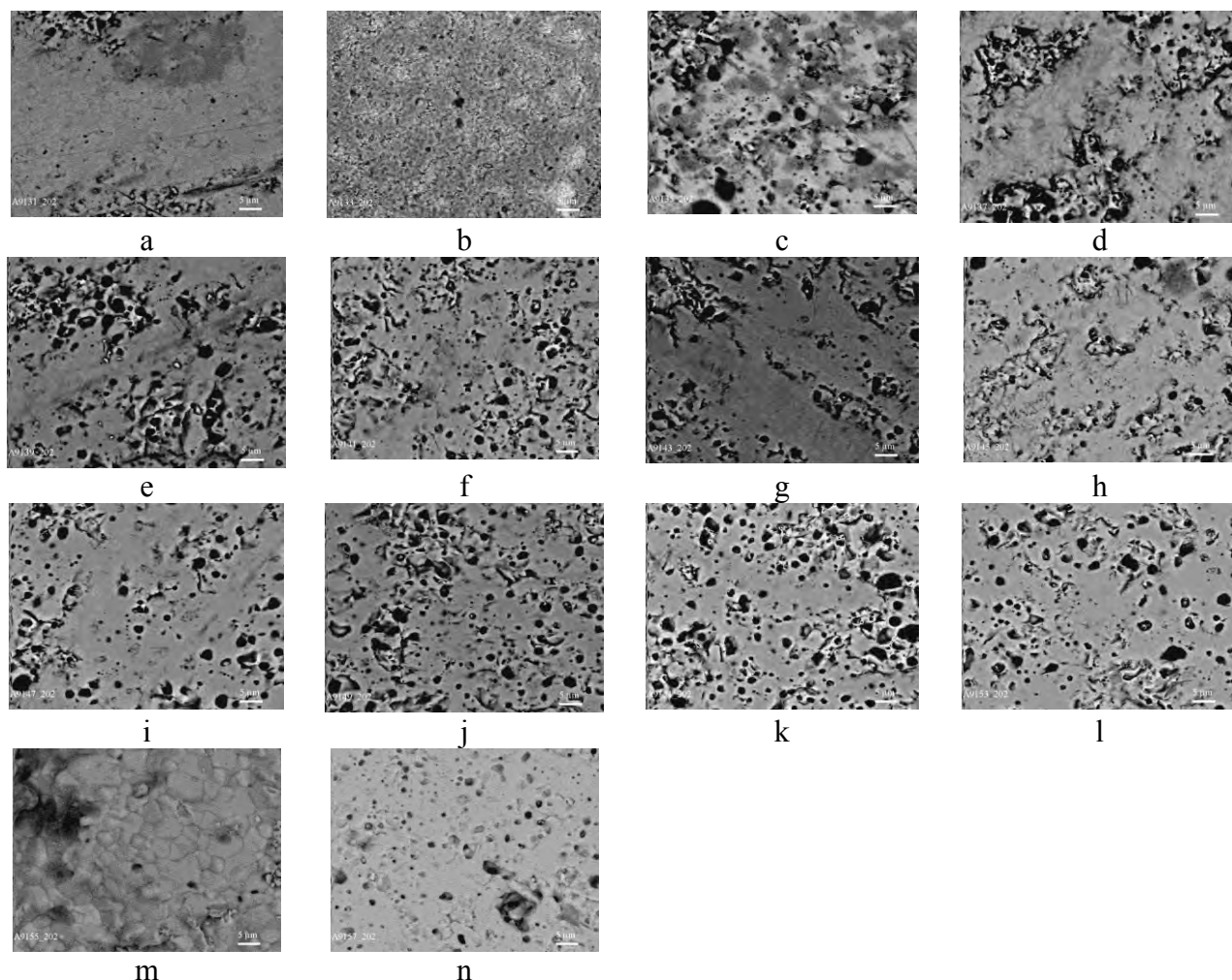
Fig 1.12 - Microstructure of samples in the CeO_2-Eu_2O_3 system after annealing at 1500 °C:
a) 4 mol % CeO_2-96 mol % Eu_2O_3, <B-Eu_2O_3> basis + <C-Eu_2O_3>, BEI, × 2000;
light phase - <B-Eu_2O_3>, gray phase (inclusions) - <C-Eu_2O_3>, black – pores;
b) 5 mol % CeO_2-95 mol % Eu_2O_3, <B-Eu_2O_3> + <C-Eu_2O_3>, BEI, × 2000;
c) 10 mol % CeO_2-90 mol % Eu_2O_3, <C-Eu_2O_3> basis + <B-Eu_2O_3>, BEI, × 2000;
d) 15 mol % CeO_2-85 mol % Eu_2O_3, <C-Eu_2O_3> basis + <B-Eu_2O_3> tr., BEI, × 2000;
e) 20 mol % CeO_2-80 mol % Eu_2O_3, <C-Eu_2O_3>, BEI, × 2000;
f) 25 mol % CeO_2-75 mol % Eu_2O_3, <C-Eu_2O_3>, BEI, × 2000;
g) 30 mol % CeO_2-70 mol % Eu_2O_3, <C-Eu_2O_3> basis + <F-CeO_2> tr., BEI, × 2000;
light phase (texture) - <C-Eu_2O_3>, dark phase - <F-CeO_2>, black – pores;
h) 35 mol % CeO_2-65 mol % Eu_2O_3, <C-Eu_2O_3> + <F-CeO_2>, BEI, × 2000;
light phase - <C-Eu_2O_3>, dark gray phases (inclusions) - <F-CeO_2>, black – pores;
i) 40 mol % CeO_2-60 mol % Eu_2O_3, <C-Eu_2O_3> basis + <F-CeO_2> tr., BEI, × 2000;
j) 45 mol % CeO_2-55 mol % Eu_2O_3, <C-Eu_2O_3> basis + <F-CeO_2> ↑, BEI, × 2000;
k) 50 mol % CeO_2-50 mol % Eu_2O_3, <C-Eu_2O_3> basis + <F-CeO_2> tr. ↑, BEI, × 2000;
l) 55 mol % CeO_2-45 mol % Eu_2O_3, <C-Eu_2O_3> basis + <F-CeO_2> tr. ↑, BEI, × 2000;
m) 60 mol % CeO_2-40 mol % Eu_2O_3, <C-Eu_2O_3> ↓ + <F-CeO_2> ↑, BEI, × 2000;
grains on fracture - <F-CeO_2>;
n) 65 mol % CeO_2-35 mol % Eu_2O_3, <F-CeO_2> basis + <C-Eu_2O_3> ↓, BEI, × 2000;
light phase - <C-Eu_2O_3>, dark phase and grains on fractures - <F-CeO_2>, black – pores;

     The microstructure research data are confirmed by the XRD results (Table. 1. 6). Increase in ceria concentration from 35 to 55 mol% CeO_2 in two-phase samples (C + F) results in the porosity

increase and complication of a relief of the surface, and inhomogeneous phase distribution (Fig. 1.12 h-l). The microstructure of two phase sample containing 60 mol % CeO_2-40 mol% Eu_2O_3 is developing as polyhedral grains of F-CeO_2 of 0.8-9.2 μm in size (Fig. 1.12 m). In the two-phase samples, containing 65-75 mol% CeO_2, the cubic modifications of F-CeO_2 represents the matrix phase (Table. 1.6). Two phases are clearly seen on microstructure: the grains of ceria look like inclusions on the fracture surfaces (Fig. 1.12 n). Note, the higher is the ceria content, the finer become grains of the F-phase.

The size of homogeneity field of the B-Eu_2O_3 solid solution at temperature 1100 °C remains quite small (< 1 mol%). The substitution of ions Eu^{3+} (r = 0.0985 nm) by smaller size ions Ce^{4+} (r = 0.090 nm) did not lead to stabilization of the B-Eu_2O_3 and solubility at 1500 °C was not increased. The same sterical factor explains larger expansion of the F-CeO_2 phase field as compared to B-phase field, which remains unchanged in the temperature range 1500-1100 °C of about 20 mol% (Fig. 1.10).

The specificity of the B-Eu_2O_3 microstructure concerns non-isometric grains from 0.42 μm to 6.7 μm long and groups of agglomerates are shown in Fig. 1.13 a. In the sample 1 mol% CeO_2-99 mol% Eu_2O_3, the fine grain two phase structure is observed, where gray phase is the main component - cubic C-Eu_2O_3 confirmed by XRD and petrography data (Table. 1.7). The monoclinic phase of B-Eu_2O_3 looks like rare light inclusions (Figs. 1.13 b). In the one-phase samples containing from 2 to 5 mol% CeO_2 and annealed at 1100 °C, the fine grain structure of C-Eu_2O_3 solid solutions was reported (Figs. 1.13 e-k). The two-phase field (C-Eu_2O_3 + F-CeO_2) exists in the concentration range 10-75 mol% CeO_2 at 1100 °C. In the petrography data, two cubic phases were revealed. The main phase is isotropic C-form of REO, but starting from 25 mol% CeO_2 the amount of another isotropic phase, which is F-CeO_2, starts growing (Fig. 1.13 f). In the samples containing 20 mol% CeO_2-80 mol% Eu_2O_3 and 25 mol% CeO_2-75 mol% Eu_2O_3, the fine grain structure is characterized by oriented stripes-like grains, the chain of grains, which probably belong to another phase and have 4.17-12.5 μm (Fig. 1.13 i,j). Further increasing of ceria content gives much coarser microstructure and porous grains appear (Fig. 1.13 k,l). In the sample containing 40 mol% CeO_2-60 mol% Eu_2O_3, two types of grains found: dark gray grains with smooth surface (F-CeO_2) and light gray grains with rough porous surface (C-Eu_2O_3). The microstructure of samples of the CeO_2-Eu_2O_3 system in the field with high content of ceria after annealing at 1100 °C is shown in Fig. 1.14. In the sample containing 80 mol% CeO_2, two phases are clearly seen. The matrix phase is F-CeO_2 solid solution, but amount of another phase C-Eu_2O_3 decreases (Fig. 1.14 g,h). Further increase of CeO_2 content happens in the solid solution (F-CeO_2) just changing surface morphology. The samples containing 90-95 mol% CeO_2 show fine grain microstructure, which includes grains and agglomerates. (Fig. 1.14 k,l).

The microstructure of some samples of the CeO_2-Eu_2O_3 system as-annealed at 600 °C were studied but no shown here. In spite of extremely durable isothermal exposure for 33061 hours at 600 °C, dense sintered samples were not obtained. Microstructure has been studied using polished and non-polished samples. As a result, the samples are substantially different by morphology and texture as compared to the samples obtained under higher temperatures (1100, 1500 °C). In the samples containing 1 mol% CeO_2-99 mol% Eu_2O_3 and 2 mol% CeO_2-98 mol% Eu_2O_3, one isotropic phase yellowish and porous C-Eu_2O_3 exists by petrography data and confirmed by XRD data and electron microscopy (Table. 1.8). The polyhedral grains of cubic modification (C) of europia are the plate-shape of different size (0.8-11.7 μ). Grain growth occurs by recrystallization in the solid phase. The traces of another isotropic phase <F-CeO_2> but with higher refraction index than for <C-Eu_2O_3> have been found in the sample 3 mol% CeO_2-97 mol% Eu_2O_3. In the electron microscopy images, the matrix phase of light color grains <C-Eu_2O_3> includes dark-phase grains of <F-CeO_2>.

The microstructures of two-phase samples containing from 4 to 45 mol% CeO_2 are representative for <C-Eu_2O_3>, where this phase is the main one. Further increase of ceria in the composition corresponds to decreasing of <C-Eu_2O_3> grains and increasing of <F-CeO_2> grains. In

the samples containing 75-85 mol % CeO$_2$, the main phase becomes <F-CeO$_2$> (Table. 1.8). The boundary solubility of Eu$_2$O$_3$ in cubic phase F-CeO$_2$ at temperature 600 °C achieves 10 mol%. The lattice parameters increases from a=0.5409 nm for pure CeO$_2$ to a=0.5418 nm (600 °C) in boundary solid solution.
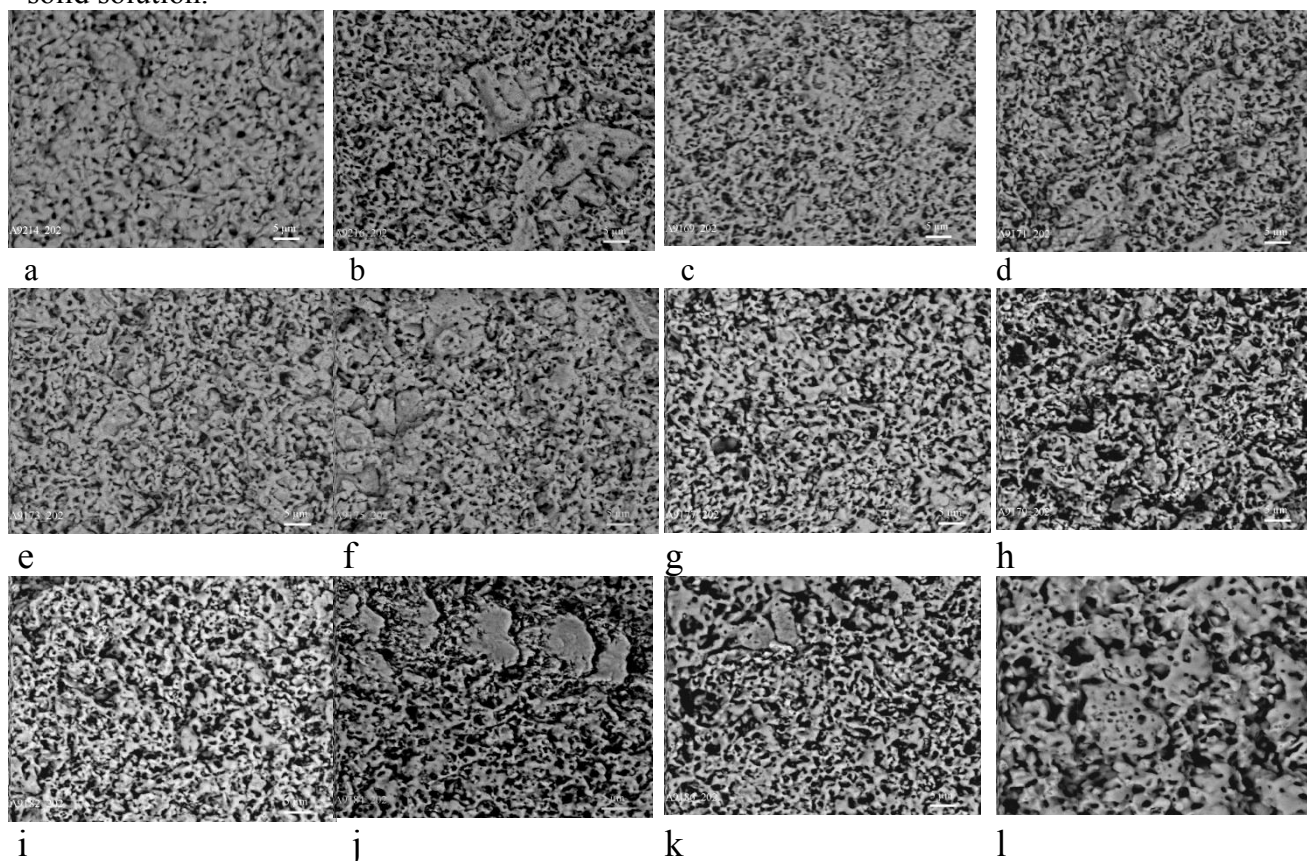

Fig 1.13 - Microstructure of the samples of the system CeO$_2$-Eu$_2$O$_3$ in the field with high amount of europia after annealing at 1100 °C:
a) 100 mol % Eu$_2$O$_3$, <B-Eu$_2$O$_3$>, BEI, × 2000; gray - <C-Eu$_2$O$_3$>;
b) 1 mol% CeO$_2$-99 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> basis + <B-Eu$_2$O$_3$> tr. l, BEI, × 2000;
c) 2 mol% CeO$_2$-98 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$>, BEI, × 2000;
d) 3 mol% CeO$_2$-97 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$>, BEI, × 2000;
e) 4 mol% CeO$_2$-96 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$>, BEI, × 2000;
f) 5 mol% CeO$_2$-95 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$>, BEI, × 2000;
g) 10 mol% CeO$_2$-90 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> basis + <F-CeO$_2$> tr., BEI, × 2000;
h) 15 mol% CeO$_2$-85 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> basis + <F-CeO$_2$>, BEI, × 2000;
i) 20 mol% CeO$_2$-80 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> basis + <F-CeO$_2$>, BEI, × 2000;
j) 25 mol% CeO$_2$-75 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> basis + <F-CeO$_2$> ↑, BEI, × 2000;
k) 30 mol% CeO$_2$-70 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> basis + <F-CeO$_2$>, BEI, × 2000;
l) 35 mol% CeO$_2$-65 mol% Eu$_2$O$_3$, <C-Eu$_2$O$_3$> + <F-CeO$_2$>, BEI, × 2000;
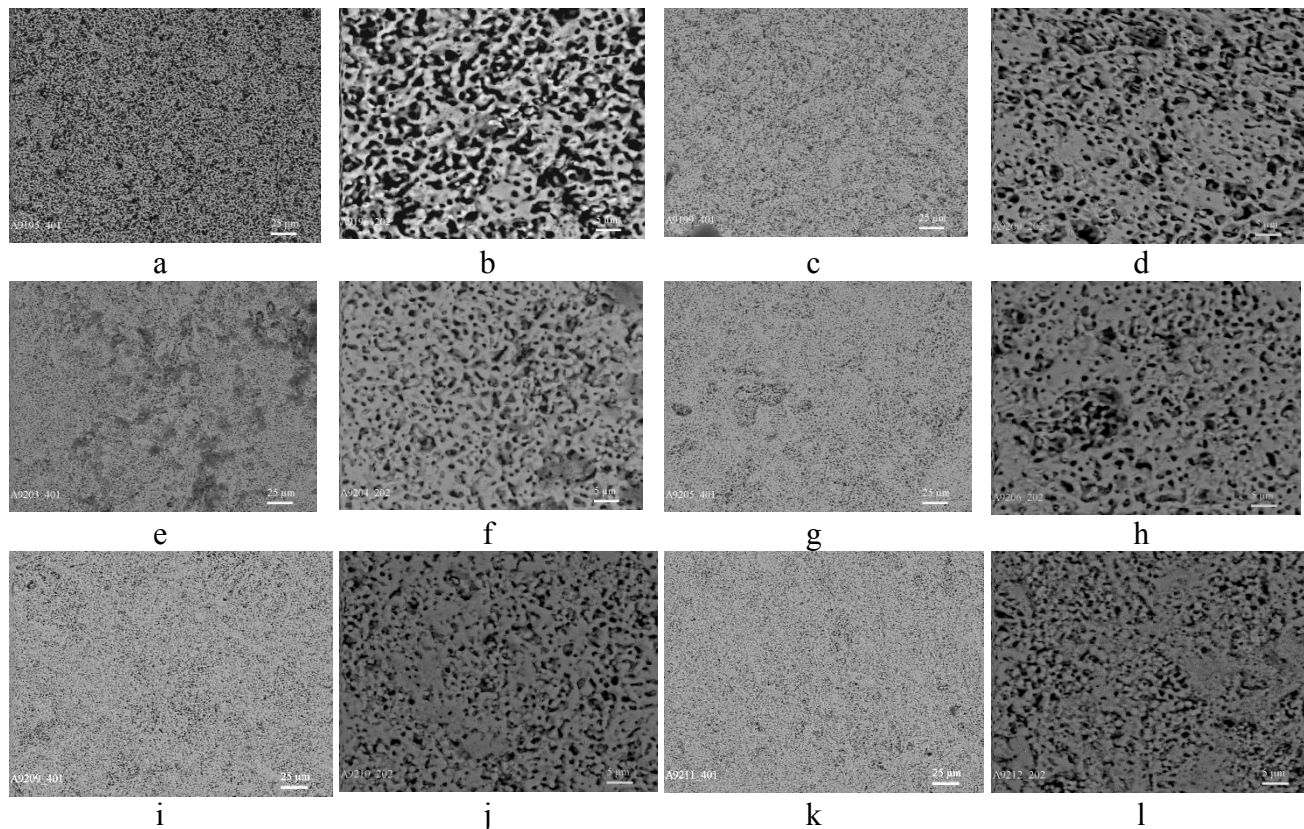light phase - <C-Eu$_2$O$_3$>, dark gray phase - <F-CeO$_2$>, black – pores;

Fig. 1.14 - Microstructure of samples in the CeO_2-Eu_2O_3 system in the field of high ceria content after annealing at 1100 °C:

a) 55 mol % CeO_2-45 mol % Eu_2O_3, <C-Eu_2O_3> ↓ + <F-CeO_2> tr. ↑, BEI, × 400;

b) 55 mol % CeO_2-45 mol % Eu_2O_3, <C-Eu_2O_3> ↓ + <F-CeO_2> tr. ↑, BEI, × 2000;

c) 65 mol % CeO_2-35 mol % Eu_2O_3, <F-CeO_2> basis ↑ + <C-Eu_2O_3> ↓↓, BEI, × 400;
light phase - <C-Eu_2O_3>, dark phase - <F-CeO_2>, black – pores;

d) 65 mol % CeO_2-35 mol % Eu_2O_3, <F-CeO_2> basis ↑ + <C-Eu_2O_3> ↓↓, BEI, × 2000;

e) 75 mol % CeO_2-25 mol % Eu_2O_3, <F-CeO_2> + <C-Eu_2O_3>, BEI, × 400;

f) 75 mol % CeO_2-25 mol % Eu_2O_3, <F-CeO_2> + <C-Eu_2O_3>, BEI, × 2000;

g) 80 mol % CeO_2-20 mol % Eu_2O_3, <F-CeO_2> + <C-Eu_2O_3> ↓, BEI, × 400;

h) 80 mol % CeO_2-20 mol % Eu_2O_3, <F-CeO_2> + <C-Eu_2O_3> ↓, BEI, × 2000;

i) 90 mol % CeO_2-10 mol % Eu_2O_3, <F-CeO_2>, BEI, × 400;

j) 90 mol % CeO_2-10 mol % Eu_2O_3, <F-CeO_2>, BEI, × 2000;

k) 95 mol % CeO_2-5 mol % Eu_2O_3, <F-CeO_2>, BEI, × 400;

l) 95 mol % CeO_2-5 mol % Eu_2O_3, <F-CeO_2>, BEI, × 2000.

Isothermal section of the phase diagram in the ZrO_2-CeO_2-Eu_2O_3 system at temperature of 1500 °C

In the ternary system ZrO_2-CeO_2-Eu_2O_3 at 1500 °C, no new phases were found. The character of phase equilibria in this system is completely determined by constitution of boundary binary system. At 1500 °C in the ZrO_2-CeO_2-Eu_2O_3 system the following one-phase fields of solid solutions have been established: tetragonal (T) and cubic (F) of fluorite type ZrO_2, monoclinic (B) and cubic (C) modifications of Eu_2O_3, cubic phase of fluorite-type (F) CeO_2 and the ordered pyrochlore-type phase of $Eu_2Zr_2O_7$ (Py).

Obtained results allowed developing a isothermal section for the ZrO_2-CeO_2-Eu_2O_3 system at 1500 °C (Fig. 1.15). The input chemical compositions and phase compositions of the samples

annealed at 1500 °C, lattice parameters of equilibrium phases at given temperatures, are presented in Table 1.10.

Table 1.10 – Chemical and phase composition, lattice parameters of phases in the ZrO_2-CeO_2-Eu_2O_3 system after annealing at 1500 °C, 150 hour. (XRD, petrography and microscopy data)

Chemical composition, mol. %			Phase compositions and parameters of elementary cells, nm ($a \pm 0.0002$)
ZrO_2	CeO_2	Eu_2O_3	
1	2	3	4
Section ZrO_2 - (50 mol % CeO_2 - 50 mol % Eu_2O_3)			
5	47.5	47.5	$<$F-$CeO_2$$>$ ($a = 0.5432$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0864$)
10	45	45	$<$F-$CeO_2$$>$ ($a = 0.5397$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0794$)
15	42.5	42.5	$<$F-$CeO_2$$>$ ($a = 0.5409$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0827$)
20	40	40	$<$F-$CeO_2$$>$ ($a = 0.5392$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0807$)
25	37.5	37.5	$<$F-$CeO_2$$>$ ($a = 0.5411$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0827$)
30	35	35	$<$F-$CeO_2$$>$ ($a = 0.5370$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0743$)
35	32.5	32.5	$<$F-$CeO_2$$>$ ($a = 0.5350$) + $<$C-$Eu_2O_3$$>$ ($a = 1.0805$) + Py tr
40	30	30	$<$F-$CeO_2$$>$ + $<$C-$Eu_2O_3$$>$ ($a = 1.0894$) + Py
45	27.5	27.5	$<$F-$CeO_2$$>$ + $<$C-$Eu_2O_3$$>$ + Py
50	25	25	$<$F-$CeO_2$$>$ + $<$C-$Eu_2O_3$$>$ + Py
55	22.5	22.5	$<$F-$CeO_2$$>$ + Py + $<$C-$Eu_2O_3$$>$ tr
60	20	20	$<$F-$CeO_2$$>$ + Py
65	17.5	17.5	$<$F-$ZrO_2$$>$ + Py + $<$T-$ZrO_2$$>$*tr
70	15	15	$<$F-$ZrO_2$$>$ basis +Py + $<$T-$ZrO_2$$>$*tr
75	12.5	12.5	$<$F-$ZrO_2$$>$ basis +Py + $<$T-$ZrO_2$$>$* tr
80	10	10	Py basis + $<$T-$ZrO_2$$>$*↑
85	7.5	7.5	$<$F-$ZrO_2$$>$ basis + $<$T-$ZrO_2$$>$*↑ + Py
90	5	5	$<$F-$ZrO_2$$>$ + $<$T-$ZrO_2$$>$* basis↑
95	2.5	2.5	$<$F-$ZrO_2$$>$ + $<$T-$ZrO_2$$>$* basis↑↑
96	2	2	$<$F-$ZrO_2$$>$ + $<$T-$ZrO_2$$>$* basis↑↑
97	1.5	1.5	$<$T-$ZrO_2$$>$* basis + $<$F-$ZrO_2$$>$
98	1	1	$<$T-$ZrO_2$$>$* basis + $<$F-$ZrO_2$$>$↓
99	0.5	0.5	$<$T-$ZrO_2$$>$*
Section CeO_2 - (67 mol % ZrO_2 – 33 mol % Eu_2O_3)			
66	1	33	Py ($Eu_2Zr_2O_7$)
65	2	33	Py + $<$F-$ZrO_2$$>$
64	3	33	Py + $<$F-$ZrO_2$$>$
64	4	32	Py + $<$F-$ZrO_2$$>$
63	5	32	Py + $<$F-$ZrO_2$$>$ + $<$C-$Eu_2O_3$$>$ tr
60	10	30	Py + $<$F-$CeO_2$$>$ + $<$C-$Eu_2O_3$$>$ tr
57	15	28	Py + $<$F-$CeO_2$$>$ + $<$C-$Eu_2O_3$$>$
53	20	27	$<$F-$CeO_2$$>$ + Py + $<$C-$Eu_2O_3$$>$
47	30	23	$<$F-$CeO_2$$>$ + Py + $<$C-$Eu_2O_3$$>$
44	35	21	$<$F-$CeO_2$$>$ + Py + $<$C-$Eu_2O_3$$>$
40	40	20	$<$F-$CeO_2$$>$ + Py + $<$C-$Eu_2O_3$$>$
37	45	18	$<$F-$CeO_2$$>$ ($a = 0.5319$) + Py + $<$C-$Eu_2O_3$$>$
34	50	16	$<$F-$CeO_2$$>$ ($a = 0.5322$) + $<$C-$Eu_2O_3$$>$
30	55	15	$<$F-$CeO_2$$>$ ($a = 0.5336$) + $<$C-$Eu_2O_3$$>$
26	60	14	$<$F-$CeO_2$$>$ ($a = 0.5356$) + $<$C-$Eu_2O_3$$>$
23	65	12	$<$F-$CeO_2$$>$ ($a = 0.5368$) + $<$C-$Eu_2O_3$$>$
20	70	10	$<$F-$CeO_2$$>$ ($a = 0.5369$) + $<$C-$Eu_2O_3$$>$ tr
17	75	8	$<$F-$CeO_2$$>$ ($a = 0.5374$) + $<$C-$Eu_2O_3$$>$ tr
13.5	80	6.5	$<$F-$CeO_2$$>$ ($a = 0.5374$)
10	85	5	$<$F-$CeO_2$$>$ ($a = 0.5386$)

1	2	3	4
7	90	3	$\langle$F-CeO$_2\rangle$ ($a=0.5390$)
3	95	2	$\langle$F-CeO$_2\rangle$ ($a=0.5397$)
			Section ZrO$_2$ - (30 mol % CeO$_2$ - 70 mol % Eu$_2$O$_3$)
5	29	66	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0849$)
10	27	63	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0819$)
15	25.5	59.5	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0802$) + $\langle$F-CeO$_2\rangle$
25	22	53	$\langle$C-Eu$_2$O$_3\rangle$ ($a=1.0737$) + $\langle$F-CeO$_2\rangle$
30	21	49	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ ($a=1.0738$) + $\langle$F-CeO$_2\rangle\uparrow$ + Py tr
40	18	42	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ ($a=1.0672$) + $\langle$F-CeO$_2\rangle\uparrow\uparrow$ + Py tr
45	16.5	38.5	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ ($a=1.0657$) + $\langle$F-CeO$_2\rangle\uparrow\uparrow$ + Py tr
50	15	35	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ ($a=1.0621$) + $\langle$F-CeO$_2\rangle\uparrow\uparrow$ + Py
55	13.5	31.5	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ ($a=1.0580$) + $\langle$F-CeO$_2\rangle\uparrow\uparrow$ + Py
65	10	25	$\langle$F-CeO$_2\rangle$ + Py$\uparrow$
70	9	21	Py $\uparrow\uparrow$ + $\langle$T-ZrO$_2\rangle$
75	8.5	16.5	Py basis + $\langle$T-ZrO$_2\rangle$
80	6	14	$\langle$F-ZrO$_2\rangle$ + Py + $\langle$T-ZrO$_2\rangle$
85	5.5	9.5	$\langle$F-ZrO$_2\rangle$ + $\langle$T-ZrO$_2\rangle$* + Py tr
90	3	7	$\langle$F-ZrO$_2\rangle$ + $\langle$T-ZrO$_2\rangle$*
			Section ZrO$_2$ - (70 mol % CeO$_2$ - 30 mol % Eu$_2$O$_3$)
5	66	29	$\langle$F-CeO$_2\rangle$ basis + $\langle$C-Eu$_2$O$_3\rangle$ tr
10	63	27	$\langle$F-CeO$_2\rangle$ basis + $\langle$C-Eu$_2$O$_3\rangle$ tr
15	59.5	25.5	$\langle$F-CeO$_2\rangle$ basis + $\langle$C-Eu$_2$O$_3\rangle$
25	53	22	$\langle$F-CeO$_2\rangle$ basis + $\langle$C-Eu$_2$O$_3\rangle$
30	49	21	$\langle$F-CeO$_2\rangle$ basis + $\langle$C-Eu$_2$O$_3\rangle$ tr
40	42	18	$\langle$F-CeO$_2\rangle$ basis + $\langle$C-Eu$_2$O$_3\rangle$ tr + Py
45	38.5	16.5	Py basis + $\langle$F-CeO$_2\rangle$ + $\langle$C-Eu$_2$O$_3\rangle$ tr
50	35	15	Py basis + $\langle$F-CeO$_2\rangle$ + $\langle$C-Eu$_2$O$_3\rangle$ tr
55	31.5	13.5	Py basis + $\langle$F-CeO$_2\rangle$
65	25	10	Py + $\langle$F-CeO$_2\rangle$ + $\langle$T-ZrO$_2\rangle$* tr
70	21	9	Py + $\langle$F-CeO$_2\rangle$ + $\langle$T-ZrO$_2\rangle$* tr
75	16.5	8.5	Py + $\langle$F-CeO$_2\rangle$ + $\langle$T-ZrO$_2\rangle$* tr
80	14	6	Py + $\langle$F-CeO$_2\rangle$ basis + $\langle$T-ZrO$_2\rangle$* tr
85	9.5	5.5	$\langle$F-CeO$_2\rangle$ + $\langle$T-ZrO$_2\rangle$* $\uparrow$ + Py
90	7	3	$\langle$F-ZrO$_2\rangle\downarrow$ + $\langle$T-ZrO$_2\rangle$*$\uparrow\uparrow$
			Section ZrO$_2$ - (10 mol % CeO$_2$ - 90 mol % Eu$_2$O$_3$)
2	10	88	$\langle$C-Eu$_2$O$_3\rangle$ ($a=1.0847$) + $\langle$B-Eu$_2$O$_3\rangle$
3	10	87	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0844$) + $\langle$B-Eu$_2$O$_3\rangle$
4	9.5	86.5	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0847$) + $\langle$B-Eu$_2$O$_3\rangle$
5	9.5	85.5	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0829$) + $\langle$B-Eu$_2$O$_3\rangle$
10	9.5	80.5	$\langle$C-Eu$_2$O$_3\rangle$ basis ($a=1.0831$) + $\langle$B-Eu$_2$O$_3\rangle$ tr$\downarrow$
15	9	76	$\langle$C-Eu$_2$O$_3\rangle$ ($a=1.0806$)
25	8.5	66.5	$\langle$C-Eu$_2$O$_3\rangle$ ($a=1.0786$) + Py
30	8	62	$\langle$C-Eu$_2$O$_3\rangle$ ($a=1.0763$) + Py$\uparrow$
35	8	57	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ ($a=1.0812$) + $\langle$F-ZrO$_2\rangle\uparrow$ + Py
40	7	53	$\langle$C-Eu$_2$O$_3\rangle\downarrow$ + $\langle$F-ZrO$_2\rangle$ + Py
45	6.5	48.5	$\langle$C-Eu$_2$O$_3\rangle$ tr $\downarrow\downarrow$ + $\langle$F-ZrO$_2\rangle$ + Py
50	6	44	$\langle$C-Eu$_2$O$_3\rangle$ tr $\downarrow\downarrow$ + $\langle$F-ZrO$_2\rangle$ + Py
55	5.5	39.5	$\langle$C-Eu$_2$O$_3\rangle$ tr $\downarrow\downarrow$ + $\langle$F-ZrO$_2\rangle$ + Py
60	5	35	$\langle$C-Eu$_2$O$_3\rangle$ tr $\downarrow\downarrow$ + $\langle$F-ZrO$_2\rangle$ + Py
70	4	26	$\langle$F-ZrO$_2\rangle$ + Py
75	3	22	$\langle$F-ZrO$_2\rangle$ + Py
80	2.5	17.5	$\langle$F-ZrO$_2\rangle$
85	1.5	13.5	$\langle$F-ZrO$_2\rangle$ basis + $\langle$T-ZrO$_2\rangle$*

1	2	3	4
90	1.5	8.5	$<T-ZrO_2>^* + <F-ZrO_2>$
			Section Eu_2O_3- (60 mol % ZrO_2 - 40 mol % CeO_2)
60	40	0	$<T-ZrO_2>^{**} + <F-CeO_2>$
57	38	5	$<F-CeO_2> + Py + <T-ZrO_2>$
53.5	36.5	10	$<F-CeO_2> + Py$
39.5	25.5	35	$<F-CeO_2> + <C-Eu_2O_3> + Py$
36	24	40	$<F-CeO_2> + <C-Eu_2O_3> + Py$
9.5	5.5	85	$<B-Eu_2O_3> + <C-Eu_2O_3>$
6	4	90	$<B-Eu_2O_3> + <C-Eu_2O_3>$
3	2	95	$<B-Eu_2O_3> + <C-Eu_2O_3>$
2.5	1.5	96	$<B-Eu_2O_3> + <C-Eu_2O_3>$
2	1	97	$<B-Eu_2O_3> + <C-Eu_2O_3>$
1.5	0.5	98	$<B-Eu_2O_3> + <C-Eu_2O_3>\downarrow$
0.5	0.5	99	$<B-Eu_2O_3> + <C-Eu_2O_3>$ tr $\downarrow\downarrow$
			Iso-concentration line 20 mol % ZrO_2
20	1	79	$<C-Eu_2O_3> + <F-ZrO_2>$
20	2	78	$<C-Eu_2O_3> + <F-ZrO_2>$
20	3	77	$<C-Eu_2O_3>$ basis $+ <F-ZrO_2>$
20	4	76	$<C-Eu_2O_3> + <F-ZrO_2>$
20	10	70	$<C-Eu_2O_3> + <F-CeO_2>$
20	20	60	$<C-Eu_2O_3> + <F-CeO_2>$
20	25	55	$<C-Eu_2O_3> + <F-CeO_2>$
20	30	50	$<C-Eu_2O_3> + <F-CeO_2>$ basis
20	35	45	$<C-Eu_2O_3> + <F-CeO_2>$
20	45	35	$<C-Eu_2O_3> + <F-CeO_2>$
20	55	25	$<C-Eu_2O_3> + <F-CeO_2>$
20	65	15	$<C-Eu_2O_3> + <F-CeO_2>$
20	75	5	$<C-Eu_2O_3> + <F-CeO_2>$
20	80	0	$<F-CeO_2>$
			Iso-concentration line 45 mol % ZrO_2
45	1	54	-
45	2	53	$<F-ZrO_2> + <C-Eu_2O_3>$
45	3	62	$<F-ZrO_2> + <C-Eu_2O_3>$
45	4	51	$<F-ZrO_2> + <C-Eu_2O_3>$
45	5	50	$<F-ZrO_2> + <C-Eu_2O_3> + Py$ tr
45	20	35	$<F-CeO_2> + <C-Eu_2O_3>$ tr $+ Py$ tr
45	45	10	$<F-CeO_2> + <C-Eu_2O_3>$ tr $+ Py$ tr
45	50	5	$<F-CeO_2> + <C-Eu_2O_3>$ tr $+ Py$ tr
45	55	0	$<F-ZrO_2> + <T-ZrO_2>^*$
			Iso-concentration line 85 mol % ZrO_2
85	0	15	$<F-ZrO_2>$
85	11	4	$<F-CeO_2> + <T-ZrO_2>^* + Py$ tr
85	12	3	$<F-CeO_2> + <T-ZrO_2>^* + Py$ tr
85	13	2	$<F-CeO_2>\downarrow + <T-ZrO_2>^{**}\uparrow + Py$ tr$\downarrow$
85	14	1	$<F-CeO_2>\downarrow\downarrow + <T-ZrO_2>^{**}$ basis$\uparrow$
85	15	0	$<T-ZrO_2>^{**}$

* Under given conditions (T=1500 °C, 150 hours, in air, slow cooling) tetragonal phase T-ZrO_2 is not stable, The monoclinic phase M-ZrO_2 is stable instead;
** Partial stabilization of T- ZrO_2 observed.

To determine the coordinates of the boundaries for the phase fields the concentration dependences of the lattice parameters were calculated (Fig. 1.16-1.18).
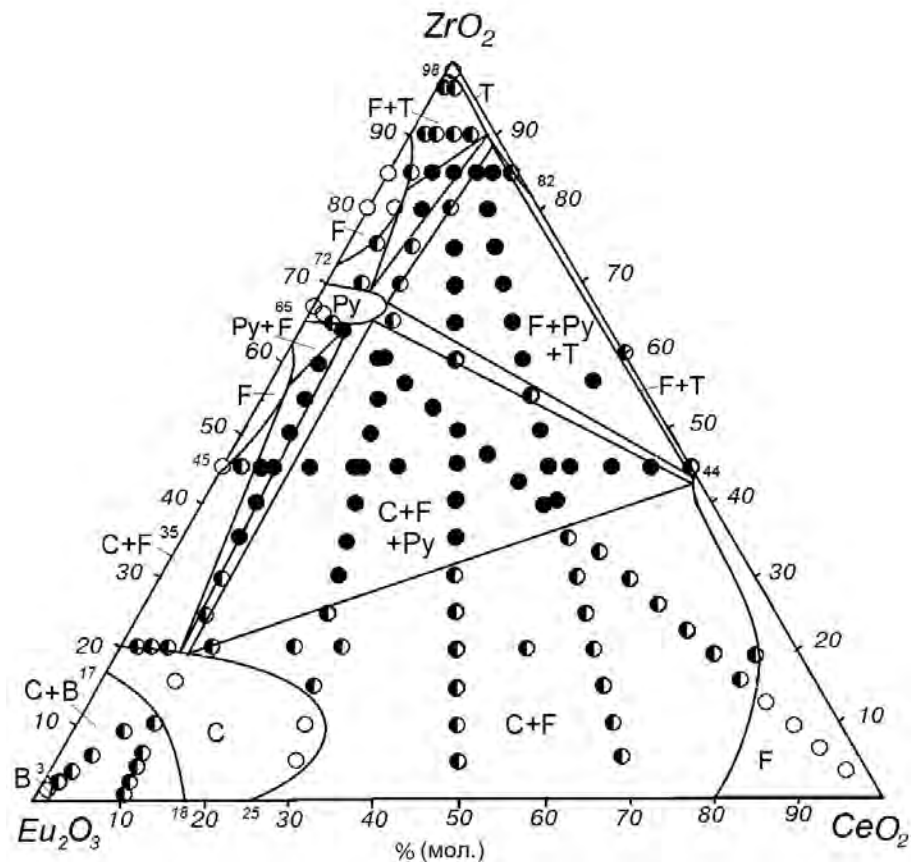
(○ – one-phase, ◑ - two-phase, ● – three-phase)

Fig. 1.15 – Isothermal cross section of the phase diagram ZrO_2-CeO_2-Eu_2O_3 at temperature 1500 °C

Using the calculated lattice parameters of the pyrochlore phase Py in the ternary fields, and data of XRD and electron microscopy, the coordinates of configurative points for Py-phase – tops of tie-line triangles (Py+T+F-CeO_2), (Py+T+F-ZrO_2), (Py+C+F-ZrO_2) and (Py+C+F-CeO_2) were determined (Table. 1.11).

Table 1.11 - Coordinates of the tie-line triangles in the system ZrO_2-CeO_2-Eu_2O_3 after annealing at 1500 °C

Phase field	Coordinates of the tie-line triangles, mol. %									
	T		Py		F-CeO_2		F-ZrO_2		C	
	ZrO_2	CeO_2	ZrO_2	CeO_2	ZrO_2	CeO_2	ZrO_2	CeO_2	ZrO_2	CeO_2
Py+T+F-CeO_2	88	10	67	7	43	56	-	-	-	-
Py+T+F-ZrO_2	90	8	68	5	-	-	83	3	-	-
Py+C+F-ZrO_2	-	-	65	5	-	-	57	2	19	6
Py+C+F-CeO_2	-	-	66	10	42	56	-	-	19	8

The typical microstructures of the samples which are in the different phase fields of the diagram of the ZrO_2-CeO_2-Eu_2O_3 system at 1500 °C are plotted on the Fig. 1.19,1.20.

Seven homogeneity fields of solid solutions were determined at 1500 °C: T- and F-form of ZrO_2, F-CeO_2, C- and B-Eu_2O_3, as well as intermediate europium zirconate $Eu_2Zr_2O_7$ (Py). The phase equilibria in this system were shown to describe reactions in solid state only.
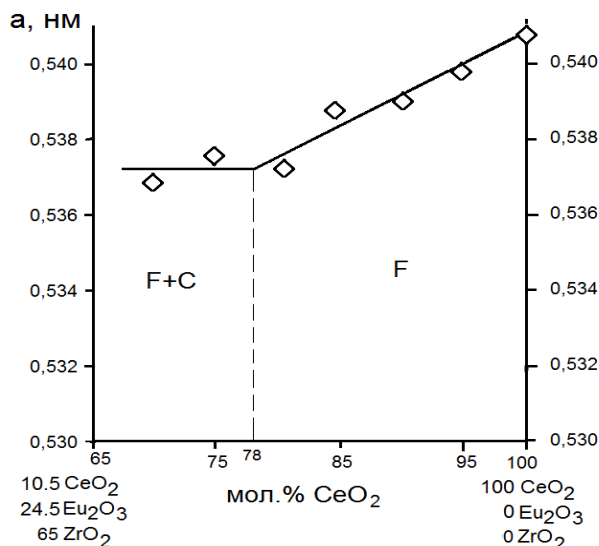
Fig. 1.16 – Concentration dependence of lattice parameter for solid solutions of fluorite type (F-CeO$_2$, ◇) by the section CeO$_2$ - (67 mol % ZrO$_2$ - 33 mol % Eu$_2$O$_3$) in the system ZrO$_2$-CeO$_2$- Eu$_2$O$_3$ after annealing at 1500 °C
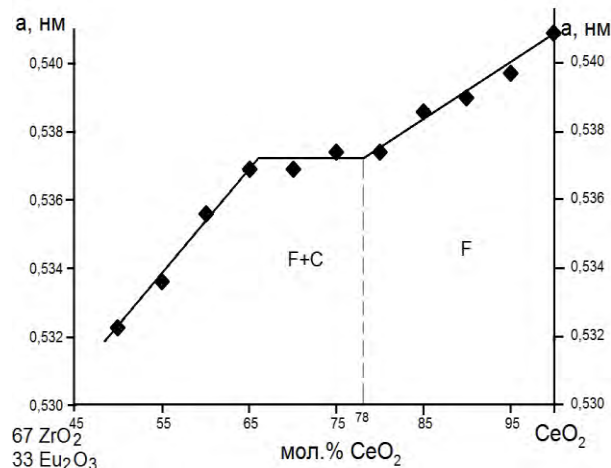
Fig. 1.16a - Concentration dependence of lattice parameter for solid solutions of fluorite type (F-CeO$_2$), ◆) by the section of CeO$_2$ - (67 mol % ZrO$_2$ - 33 mol % Eu$_2$O$_3$) in the system ZrO$_2$-CeO$_2$- Eu$_2$O$_3$ after annealing at 1500 °C
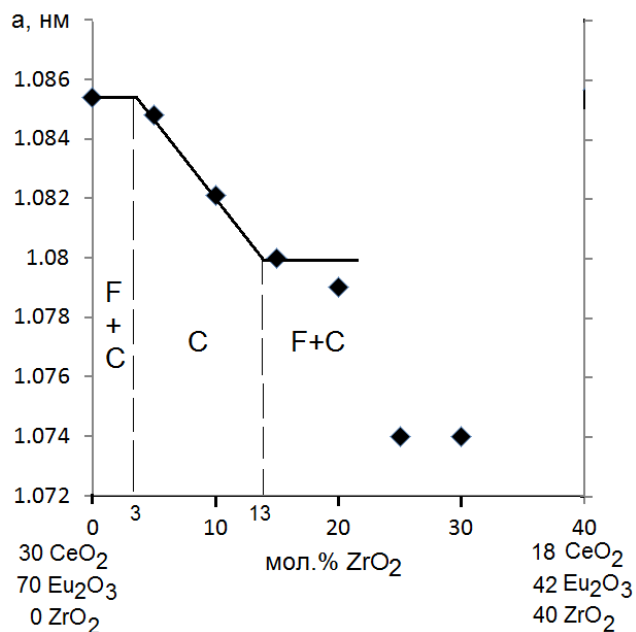
Fig. 1.17 - Concentration dependence of lattice parameter for solid solutions of the C type of REO (C-Eu$_2$O$_3$, ◆) by section ZrO$_2$ - (30 mol % CeO$_2$ - 70 mol % Eu$_2$O$_3$) in the system ZrO$_2$-CeO$_2$-Eu$_2$O$_3$ after annealing at 1500 °C
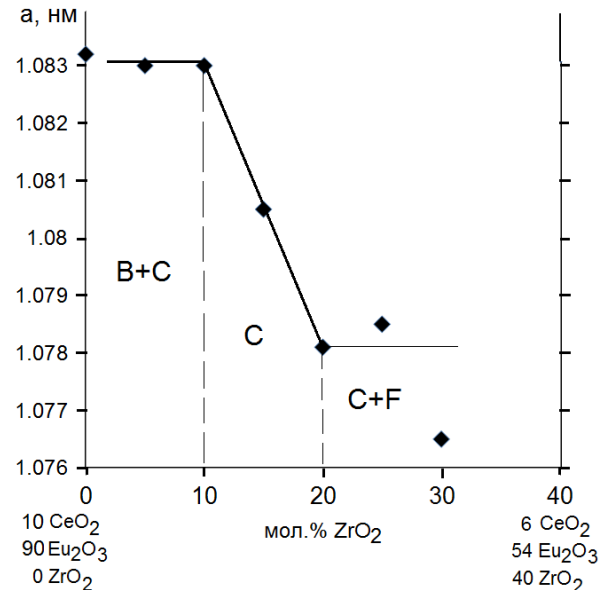
Fig. 1.18 - Concentration dependence of lattice parameter for solid solutions of C type REO (C-Eu$_2$O$_3$, ◆) by the section of ZrO$_2$ - (10 mol % CeO$_2$ - 90 mol % Eu$_2$O$_3$) in the system ZrO$_2$-CeO$_2$-Eu$_2$O$_3$ after annealing at 1500 °C

In the area of high zirconia content, the solid solutions based on tetragonal modification of ZrO$_2$, cubic pyrochlore-type phase Eu$_2$Zr$_2$O$_7$ and and cubic fluorite-type phases based on zirconia and ceria. The narrow field of tetragonal zirconia solid solutions is drawn out the boundary binary system ZrO$_2$-CeO$_2$ (0-18 mol% CeO$_2$). The solubility of Eu$_2$O$_3$ in the T-ZrO$_2$ is limited, about 1 mol %, which is confirmed by XRD data. The boundary of the homogeneity field of the solid solution based on tetragonal T-ZrO$_2$ at 1500 °C goes close to the following samples: 98 mol%

ZrO_2-1 mol % CeO_2-1 mol % Eu_2O_3, 90 mol % ZrO_2-7 mol % CeO_2-3 mol % Eu_2O_3, 85 mol % ZrO_2-14 mol % CeO_2-1 mol % Eu_2O_3 – two-phase (T + F), 85 mol % ZrO_2-9.5 mol % CeO_2-5.5 mol % Eu_2O_3 – three-phase (T+F+Py). In the ternary system, ceria and europia dissolve in the tetragonal zirconia approximately in the same amount as in the boundary binary systems ZrO_2-Eu_2O_3 and ZrO_2-CeO_2. It is worth noting, that the solid solutions based on T- ZrO_2 cannot be fixed on quenching at any cooling rates. The x-ray diffraction patterns recorded at room temperatures show lines, attributed to M-ZrO_2. Для ряду складів спостерігали The partial stabilization of T-phase has been observed in a number of samples (Table. 1.10). Fully stabilized tetragonal phase T-ZrO_2 was found in the two and three phase samples along the section ZrO_2 - (70 mol % CeO_2 - 30 mol % Eu_2O_3) or in the samples containing 70 mol % ZrO_2-9 mol % CeO_2-21 mol % Eu_2O_3, 75 mol % ZrO_2-8.5 mol % CeO_2-16.5 mol % Eu_2O_3, 80 mol % ZrO_2-6 mol % CeO_2-14 mol % Eu_2O_3.

Petrography allows revealing the phase transitions due to polysynthetic twinning. Microstructure of the solid solutions based on T* - zirconia for sample containing 99 mol % ZrO_2-0.5 mol % CeO_2-0.5 mol % Eu_2O_3 is identified as smooth component. The solid solution based on europium zirconate at 1500 °C is in equilibrium with all phases existing in the system ZrO_2-CeO_2-Eu_2O_3, excluding monoclinic B-europia. The field of solid solutions based on pyrochlore phase Py is directed to the side of boundary binary system ZrO_2-CeO_2. The maximum solubility of ceria in $Eu_2Zr_2O_7$ achieves 7 mol % CeO_2 (Table 1.10) along the iso-concentration line of 67 mol % ZrO_2, because the ion size is Ce^{4+} (r=0.090 nm), which is intermediate between ion sizes of Eu^{3+} (r=0.0985 nm) and Zr^{4+} (r=0.079 nm) [24]. The microstructure of solid solution based on the pyrochlore-type phase consists of randomly oriented grains, which is not typical for this phase (Fig. 1.19 a). The microstructure of the one-phase sample containing 66 mol % ZrO_2-1 mol % CeO_2-33 mol % Eu_2O_3 is presented by fine (0.8-10.8 μm) polyhedral grains clearly faceted (Fig. 1.19 a). The micro-x-ray spectral analysis showed, that the sample is one-phase, all elements (Zr, Eu) are uniformly distributes along the surface. This coincides with XRD data to confirm the solid solution formation based on ordered phase $Eu_2Zr_2O_7$ (Py) (Table. 1.10). The microstructures of the samples characterizing the two-phase field (Py + F-ZrO_2) are presented in the Fig. 1.19 b-d, 1.20 a-d. In the samples, containing 65 mol % ZrO_2-2 mol % CeO_2-33 mol % Eu_2O_3, 64 mol % ZrO_2-3 mol % CeO_2-33 mol % Eu_2O_3 i 64 mol % ZrO_2-4 mol % CeO_2-32 mol % Eu_2O_3 one can find two structural components, different by contrast (Fig. 1.19 b-d). The light phase is mainly represented by grains of 2.5-15.8 μm in size (Fig. 1.19 c), the dark phase – by grains of 1.7-2.1 μm in size (Fig. 1.19 b). In accordance with micro-x-ray spectral analysis data the dark phase contains zirconia only and, therefore, it could be F-ZrO_2 phase, while the gray phase was enriched with europium and zirconium. It could be identified as pyrochlore-type $Eu_2Zr_2O_7$ (Py) phase, which has been proved by XRD and petrography. An increase of ZrO_2 amount leads to increase of the pyrochlore phase volume and changes in morphology of grains. When ceria concentration increased, on the definite microsections of the sample 64 mol % ZrO_2-4 mol % CeO_2-32 mol % Eu_2O_3 it becomes obviously seen the refining of grains, increasing of fragility and development of crack network inside the grains (Fig. 1.19 d). In accordance with petrography data, the isotropic phases of two types were observed: the isotropic matrix phase of pyrochlore (Py) coexists with the second phase of fluorite-type (F), which is substantially less. By the cross section of CeO_2 - (67 mol % ZrO_2 – 33 mol % Eu_2O_3) in the samples containing 2-4 mol % CeO_2 one clearly finds two-phase finegrain structure, consisting of isotropic phase of pyrochlore type and locally dispersed particles of the second isotropic fluorite-type phase. The character of the two-phase microstructure (Py + F-ZrO_2), containing 70 mol % ZrO_2-4 mol % CeO_2-26 mol % Eu_2O_3, 75 mol % ZrO_2-3 mol % CeO_2-22 mol % Eu_2O_3 by the cross section ZrO_2 - (10 mol % CeO_2 - 90 mol % Eu_2O_3) substantially differs by morpholody and properties (Fig. 1.20 a-d). The structure in these samples is developing as a porous and dense smooth fragments of the surfaces, where gray, smooth one belongs to <F-ZrO_2>, and gray, porous one belongs to pyrochlore $Eu_2Zr_2O_7$ (Py).
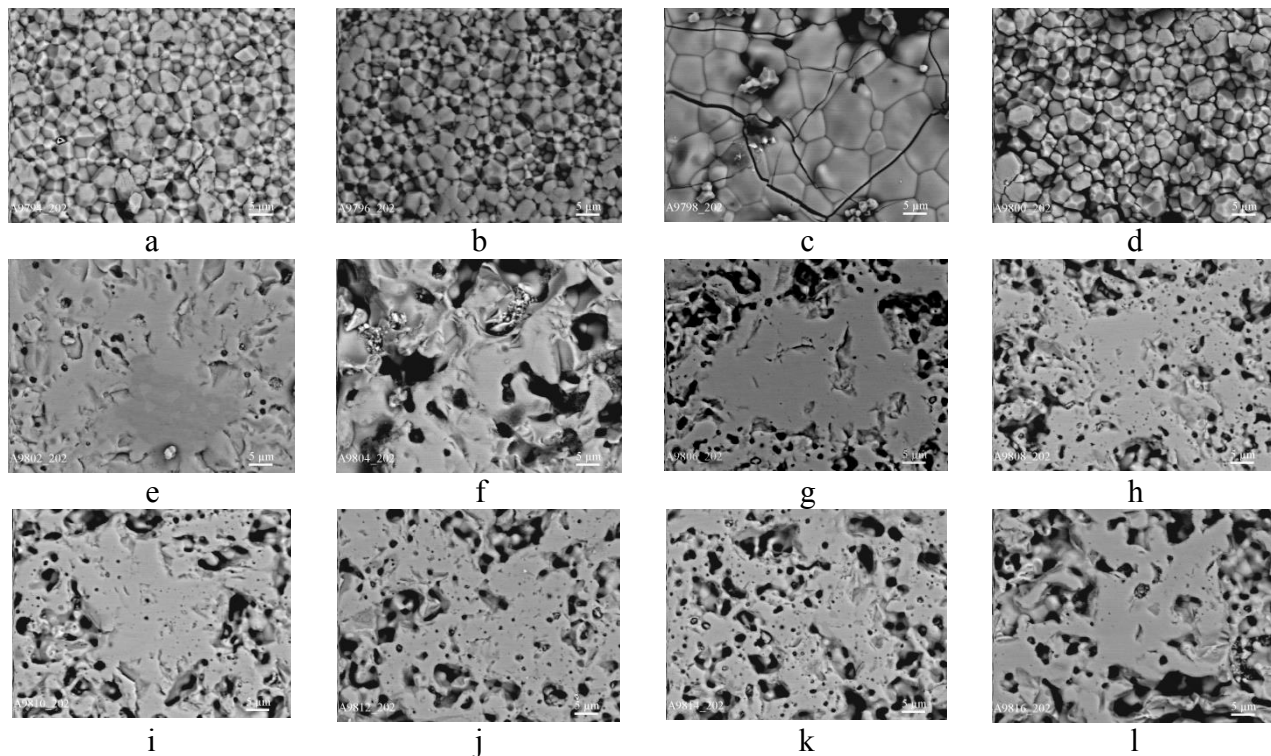
Fig. 1.19 – Microstructure of the samples in the system ZrO_2-CeO_2-Eu_2O_3 along the cross-section CeO_2 - (67 mol % ZrO_2 - 33 mol % Eu_2O_3) after annealing at 1500 °C:

a) 66 mol % ZrO_2-1 mol % CeO_2-33 mol % Eu_2O_3, Py ($Eu_2Zr_2O_7$), BEI, × 2000;

b) 65 mol % ZrO_2-2 mol % CeO_2-33 mol % Eu_2O_3, Py + <F-ZrO_2>, BEI, × 2000;
gray gains - $Eu_2Zr_2O_7$ (Py), dark grains - <F-ZrO_2>;

c) 64 mol % ZrO_2-3 mol % CeO_2-33 mol % Eu_2O_3, Py + <F-ZrO_2>, BEI, × 2000;
grains - $Eu_2Zr_2O_7$ (Py), gray phase – Py, dark phase - <F-ZrO_2>, black – pores;

d) 64 mol % ZrO_2-4 mol % CeO_2-32 mol % Eu_2O_3, Py + <F-ZrO_2>, BEI, × 2000;

e) 63 mol % ZrO_2-5 mol % CeO_2-32 mol % Eu_2O_3, Py basis + <F-ZrO_2> + <C-Eu_2O_3> tr., BEI, × 2000;
light gray (matrix) - $Eu_2Zr_2O_7$ (Py), dark gray (inclusions) - <F-ZrO_2>, light phase (small inclusions in dark matrix) - <C-Eu_2O_3> tr., black – pores;

f) 60 mol % ZrO_2-10 mol % CeO_2-30 mol % Eu_2O_3, Py + <F-CeO_2> + <C-Eu_2O_3> tr., BEI, × 2000;

g) 57 mol % ZrO_2-15 mol % CeO_2-28 mol % Eu_2O_3, Py + <F-CeO_2> + <C-Eu_2O_3>, BEI, × 2000;
gray phase - <F-CeO_2>, gray porous phase - Py, light phase (smll grain inclusions), crushed phase - <C-Eu_2O_3>, black – pores;

h) 53 mol % ZrO_2-20 mol % CeO_2-27 mol % Eu_2O_3, <F-CeO_2> + Py + <C-Eu_2O_3>, BEI, × 2000;

i) 47 mol % ZrO_2-30 mol % CeO_2-23 mol % Eu_2O_3, <F-CeO_2> + Py + <C-Eu_2O_3>, BEI, × 2000;

j) 44 mol % ZrO_2-35 mol % CeO_2-21 mol % Eu_2O_3, <F-CeO_2> + Py + <C-Eu_2O_3>, BEI, × 2000;

k) 40 mol % ZrO_2-40 mol % CeO_2-20 mol % Eu_2O_3, <F-CeO_2> + Py + <C-Eu_2O_3>, BEI, × 2000;

l) 37 mol % ZrO_2-45 mol % CeO_2-18 mol % Eu_2O_3, <F-CeO_2> basis + Py + <C-Eu_2O_3>, BEI, × 2000.

The homogeneity field grain boundaries for $Eu_2Zr_2O_7$ phase, which is in equilibria with T-ZrO_2 and C-Eu_2O_3 at 1500 °C have substantial elongation to ZrO_2-Eu_2O_3 side of concentration triangle. The microstructures of the samples containing 80 mol % ZrO_2-10 mol % CeO_2-10 mol % Eu_2O_3, 96 mol % ZrO_2-2 mol % CeO_2-2 mol % Eu_2O_3, 97 mol % ZrO_2-1.5 mol %CeO_2-1.5 mol % Eu_2O_3, 98 mol % ZrO_2-1 mol % CeO_2-1 mol % Eu_2O_3 by the section ZrO_2 - (50 mol % CeO_2 - 50 mol %

Eu_2O_3) and 70 mol % ZrO_2-9 mol % CeO_2-21 mol % Eu_2O_3, Py ↑↑ + <T-ZrO_2>, 75 mol % ZrO_2-8.5 mol % CeO_2-16.5 mol % Eu_2O_3 by the section ZrO_2 - (30 mol % CeO_2 − 70 mol % Eu_2O_3) show us that they are crystallized as two-phase compositions and accordingly to XRD, they correspond to two-phase field (Py + T) on the diagram of state. Both phases are distinct by their morphology. By the data of micro-x-ray spectral analysis the smooth gray phase is zirconia only and, obviously, corresponds to tetragonal solid solution T-ZrO_2. The gray and porous phase is enriched with europium and zirconium, thus, it relates to $Eu_2Zr_2O_7$ (Py), which is confirmed by x-ray analysis.

a

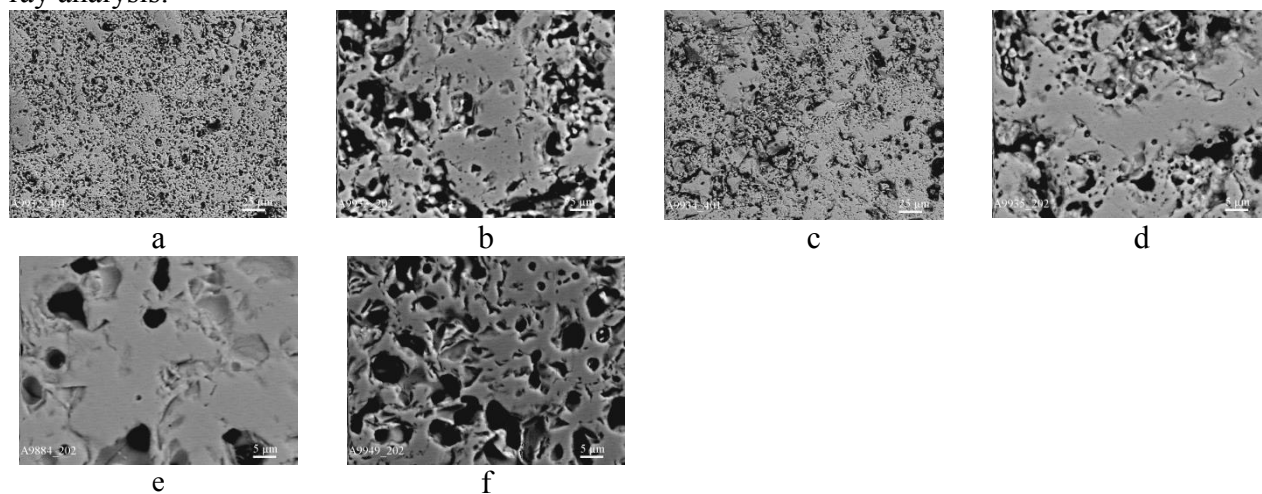b

c

d

e

f

Fig. 1.20 – Microstructure of the samples ZrO_2-CeO_2-Eu_2O_3 along the section ZrO_2 - (10 mol % CeO_2 - 90 mol % Eu_2O_3) at 1500 °C:
a) 70 mol % ZrO_2-4 mol % CeO_2-26 mol % Eu_2O_3, <F-ZrO_2> + Py, BEI, × 400;
b) 70 mol % ZrO_2-4 mol % CeO_2-26 mol % Eu_2O_3, <F-ZrO_2> + Py, BEI, × 2000;
light gray - <F-ZrO_2>, gray porous - $Eu_2Zr_2O_7$ (Py), black – pores;
c) 75 mol % ZrO_2-3 mol % CeO_2-22 mol % Eu_2O_3, <F-ZrO_2> + Py, BEI, × 400;
d) 75 mol % ZrO_2-3 mol % CeO_2-22 mol % Eu_2O_3, <F-ZrO_2> + Py, BEI, × 2000;
e) 55 mol. % ZrO_2-31.5 mol % CeO_2-13.5 mol % Eu_2O_3, Py basis + <F-CeO_2>, BEI, × 2000;
f) 53.5 mol % ZrO_2-36.5 mol % CeO_2-10 mol % Eu_2O_3, <F-CeO_2> + Py, BEI, × 2000;

The samples composed of 25 mol % ZrO_2-8.5 mol % CeO_2-66.5 mol % Eu_2O_3, 30 mol % ZrO_2-8 mol % CeO_2-62 mol % Eu_2O_3, are located along the boundary of two phase field (Py + C).
The peculiarity of the isothermal section of the phase diagram in the ZrO_2-CeO_2-Eu_2O_3 system at temperature 1500 °C is formation of phase equilibria on the basis of the fluorite solid solutions ZrO_2(CeO_2) with other components. There are at least three homogeneity fields of cubic phases. Similarly to two-component sysytem ZrO_2-Eu_2O_3, the solubility gap for homogeneity field for F-ZrO_2 phase has been observed around the $Eu_2Zr_2O_7$ phase in the ternary system. The boundaries of the homogeneity field for the F-ZrO_2 start in the boundary binary system ZrO_2-Eu_2O_3 (72-90 mol % ZrO_2 and 45-63 mol % ZrO_2). When both solid solutions of the F-type doped with ceria, its solubility does not exceed several per cents. The extension of the F-phase in the phase diagram with high content of zirconia are defined by the samples ZrO_2 - (10 mol % CeO_2-90 mol % Eu_2O_3) iso-concentration line 85 mol % ZrO_2, containing 75 mol % ZrO_2-3 mol % CeO_2-22 mol % Eu_2O_3 – two-phase (F-ZrO_2 +Py), 80 mol % ZrO_2-2.5 mol % CeO_2-17.5 mol % Eu_2O_3 – one-phase (F-ZrO_2), 85 mol % ZrO_2-1.5 mol % CeO_2-13.5 mol % Eu_2O_3 – two-phase (F-ZrO_2 + T*). In the sub-system with low content of ZrO_2, the boundary of the solid solutions based on F-ZrO_2 goes close to the sample 45 mol % ZrO_2-2 mol % CeO_2-53 mol % Eu_2O_3 – which is two-phase (F-ZrO_2 + C-Eu_2O_3) along the iso-concentration line 45 mol % ZrO_2. The solubility limit of ceria in F-ZrO_2 is about 3 and 2 mol%, respectively. The maximal extension demonstrates the homogeneity field of the solid solution based on F-CeO_2. The boundary of the F-phase field is banded to the CeO_2 corner

starting from configuration points in the binary system ZrO_2-CeO_2 (56-100 mol % CeO_2) and CeO_2-Eu_2O_3 (80-100 mol % CeO_2). And marked with the following samples 17 mol % ZrO_2-75 mol % CeO_2-8 mol % Eu_2O_3, 20 mol % ZrO_2-75 mol % CeO_2-5 mol % Eu_2O_3, 13.5 mol % ZrO_2-80 mol % CeO_2-6.5 mol % Eu_2O_3. The lattice parameters of the cubic phase is changing from a = 0.5409 nm for pure CeO_2 to a = 0.5374 nm for two-phase sample containing 17 mol % ZrO_2-75 mol % CeO_2-8 mol % Eu_2O_3.

Accordingly to micro-x-ray spectral analysis the gray, smooth grains of the phase <F-CeO_2>, gray porous structure relates to $Eu_2Zr_2O_7$. The electron microscopy data is confirmed by XRD and petrography. In the section ZrO_2-(50 mol % CeO_2-50 mol % Eu_2O_3), the sample containing 60 mol % ZrO_2-20 mol % CeO_2-20 mol % Eu_2O_3 includes two isotropic phases F-CeO_2 and $Eu_2Zr_2O_7$ in equal amount. In the sample containing 55 mol % ZrO_2-31.5 mol % CeO_2-13.5 mol % Eu_2O_3 by the section ZrO_2 - (70 mol % CeO_2 – 30 mol % Eu_2O_3) amount of the pyrochlore phase increases and morphology of samples changes. SEM images allow resolving of various phases by contrast: the pyrochlore as the substantive phase of light color contains dark inclusions of F-CeO_2 (Fig. 1.20 e). In the sample of boundary composition 53.5 mol % ZrO_2-36.5 mol % CeO_2-10 mol % Eu_2O_3, by the section of Eu_2O_3 - (60 mol % ZrO_2 – 40 mol % CeO_2), the microstructure changes its character – the porosity disappears and one smooth phase remains only forming dark gray texture of F-CeO_2 (Fig. 1.20 f).

From the results of micro-x-ray spectral analysis one can conclude, that the light-gray and a smooth phase represents F-CeO_2, the light-gray and porous is $Eu_2Zr_2O_7$, and the dark - T-ZrO_2. In the cross section ZrO_2-(70 mol % CeO_2-30 mol % Eu_2O_3), the sample 65 mol % ZrO_2-25 mol % CeO_2-10 mol % Eu_2O_3 contain two isotropic F and Py phases in equal proportion as well as traces of the T-ZrO_2 with high refraction index (n ~ 2.06). Accordingly the petrography results, the following composition 70 mol % ZrO_2-21 mol % CeO_2-9 mol % Eu_2O_3, includes two isotropic phases non-homogeneously distributed, amount of isotropic phase increases. In the sample 75 mol % ZrO_2-16.5 mol % CeO_2-8.5 mol % Eu_2O_3 the light gray and porous (Py) phase including gray inclusions (F-CeO_2) and intergrain dark-gray inclusions (T-ZrO_2). Isotropic phase (F-CeO_2) with numerical non-isotropic inclusions (T-ZrO_2) represents the matrix for composition 80 mol % ZrO_2-14 mol % CeO_2-6 mol % Eu_2O_3. Another isotropic phase of pyrochlore type (Py) is observed in smaller amount. The higher is the zirconia content, the smaller is the grain size. In the sample 85 mol % ZrO_2-9.5 mol % CeO_2-5.5 mol % Eu_2O_3 the main phase is the cubic F-CeO_2 with isotropic inclusions of $Eu_2Zr_2O_7$. The non-isotropic phase is more fine-grain. The boundaries of three-phase field (Py + F-CeO_2 + T-ZrO_2) are defined by coordinates of samples in the section Eu_2O_3 - (60 mol % ZrO_2 - 40 mol % CeO_2) and along the iso-concentration line 85 mol % ZrO_2. The isothermal section of the system ZrO_2—CeO_2—Eu_2O_3 at 1100 °C is shown in Fig. 1.21.

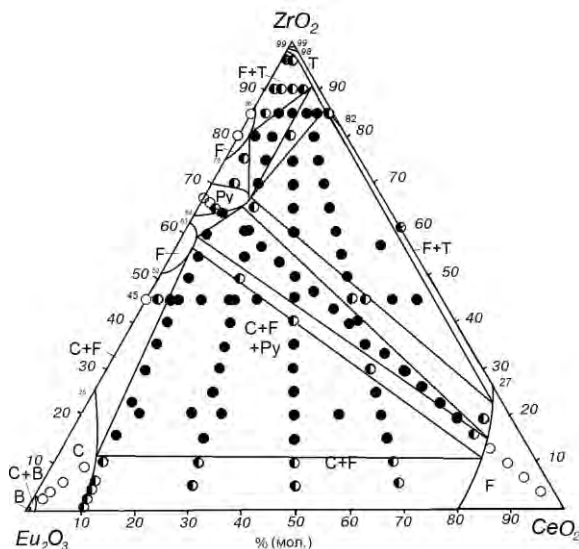Fig 1.21 - Isothermal section of the system ZrO_2—CeO_2—Eu_2O_3 at 1100 °C

1.2. Phase equilibria in the ZrO_2—CeO_2—Gd_2O_3 systems

Systems with zirconia, ceria and gadolinia should be very promising as an alternative material for the development of thermal barrier coatings and solid oxide fuel cells [1, 2]. In addition, these systems are able to be used widely in nuclear energy engineering to develop safe and reliable technologies for the waste management nuclear industry and the development of new generation reactors [3, 4]. Presently, the search of inert matrices for immobilization of plutonium is intensive. The materials for inert matrix must meet definite requirements, such as high efficiency of neutron absorption, improved thermophysical properties such as low thermal conductivity, low coefficient of thermal expansion, the absence of phase transitions and stability at high temperatures. In addition, high temperature structural ceramics with low thermal conductivity and low thermal expansion is needed for many insulation materials, as well as parts of nuclear reactors. Due to the similarity of physico-chemical properties of plutonium oxide and cerium oxide, CeO_2 is widely used as a surrogate material instead of PuO_2. Because the units are designed for plutonium ions, in the structural model of pyrochlore, the plutonium ions are substituted by cerium ions. To fix the transuranic elements, ceramic matrix represents the best choice, because there is long-term high thermodynamic stability. Crystal lattice of the pyrochlore phase ($A_2B_2O_7$) containing Zr is one of the ideal object $M_2Zr_2O_7$ (M is a three and/or four-charged cation) and reliable matrix for storage of highly concentrated nuclear wastes. Ordered phase of the pyrochlore type $Gd_2Zr_2O_7$ is also a promising material with thermal conductivity lower than stabilized zirconia has [4]. Thermal properties of rare earth zirconate used mainly in thermal barrier coatings on gas turbine blades to protect metal parts from hot gas streams [5-6]. It should be noted that composition corresponding to $Gd_2Zr_2O_7$ compound exists as disordered fluorite-type phase at high temperatures, while at low temperatures it becomes ordered pyrochlore-type structure in which oxygen vacancies and cations are ordered. The pyrochlore type phase undergoes order-disorder transition at a relatively high temperature of ~ 1550 ° C.

In addition, refractories based on zirconium dioxide stabilized by gadolinium oxide, have found usage in installations for growing single crystals of gadolinium gallium garnet. Use these refractories provides prevention of possible contamination of single crystals during merging through evaporation stabilizing additives [7, 8]. Development of ceramic technology for refractories based on ZrO_2 meets considerable difficulties because the phase diagram of the system ZrO_2-Gd_2O_3 not been studied well. Phase relations in the boundary binary systems ZrO_2-Gd_2O_3, CeO_2-Gd_2O_3 has been studied in [9, 10, 11-27]. Some of the phase relations in the ternary system ZrO_2-CeO_2-Gd_2O_3 defined in [28]. In spite of the large amount of publication on these systems, the results are contradictive yet. Thus, the study of phase equilibria in the above systems is very important and legitimate, at least to in order to determine the solubility of Ce^{4+} in $Gd_2Zr_2O_7$.

In this work first time phase equilibria are studied in the binary ZrO_2-Gd_2O_3, CeO_2-Gd_2O_3 systems in the whole interval of concentration and at temperature 1500 °C.

1.1. The system ZrO_2-Gd_2O_3

In the ZrO_2-Gd_2O_3 system at 1500 °C, there had been found fields of solid solutions based on tetragonal (T) and cubic (F) modifications of ZrO_2, monoclinic (B) and cubic (C) modifications of Gd_2O_3 and ordered phase, which crystallized in the cubic structure of pyrochlore type $Gd_2Zr_2O_7$ (Py) (Fig. 1.22). Output chemical and phase composition of the melted and annealed at 1500 °C samples, parameters of elementary cells of the phases, which are in equilibria at given temperature, given in the Tables 1.12-1.13.

To determine boundaries of the phase fields the concentration dependences of elementary cells of the phases formed (Fig. 1.23). In the field with high content of ZrO_2, the solid solutions are formed based on tetragonal ZrO_2, however the tetragonal modification of T-ZrO_2 cannot be quenched under

given conditions, and monoclinic phase M-ZrO$_2$ had been found instead. The solubility of Gd$_2$O$_3$ in T-ZrO$_2$ is bellow than 1 mol. %.

In accordance with the data (Table. 1.12), the boundaries of two-phase field (T+F) had been determined as localized between 1 and 10 mol. % Gd$_2$O$_3$ (Fig. 1.23) using the concentration dependence of lattice parameters for elementary cell of the fluorite type solid solutions. The field of the fluorite solid solutions shows a gap in the temperature and concentration intervals where the pyrochlore phase Gd$_2$Zr$_2$O$_7$ exists. The boundaries of the F phase field at 1500 °C vary between 51-57 and 74-90 mol. % ZrO$_2$. The lattice parameters of the solid solutions are growing from a = 0.5271 to a = 0.5294 and from a = 0.5148 to a = 0.5208 nm (Fig. 1.23, Table. 1.12). The homogeneity fields of the F phase are separated by narrow two-phase fields (F+Py) from ordered phase fields Gd$_2$Zr$_2$O$_7$ of the pyrochlore phase. On the diffraction patterns of the samples 72-73 mol. % ZrO$_2$ and 58-60 mol. % ZrO$_2$ the pyrochlore phase lines were found as well as fluorite phase one (F).

Boundaries of the homogeneity fields (gadolinium zirconate) pass between 29 and 38 mol. % Gd$_2$O$_3$ (1500 °C). Lattice parameters of elementary cells for the cubic solid solutions based on Gd$_2$Zr$_2$O$_7$, are growing from a=1.0426 nm for the composition 72 mol. % ZrO$_2$-28 mol. % Gd$_2$O$_3$ to a=1.0531 nm for the composition, which contains 60 mol. % ZrO$_2$-40 mol. % Gd$_2$O$_3$ (Fig. 1.2, Table. 1.12). The samples containing 25 mol. % ZrO$_2$-75 mol. % Gd$_2$O$_3$ and 51 mol. % ZrO$_2$-49 mol. % Gd$_2$O$_3$ define the boundaries of the two phase fields (C+F) at 1500 °C.

The boundaries of the homogeneity field of the C phase in equilibria with F-ZrO$_2$ and B-Gd$_2$O$_3$ at 1500 °C are elongated from 76 to 92 % Gd$_2$O$_3$. The lattice parameter of the solid solution <C-Gd$_2$O$_3$> depends on ZrO$_2$ concentration on fig. 1.2. From the presented data we enable to conclude, that the solubility of ZrO$_2$ in C-form of Gd$_2$O$_3$ achieves 24 mol. % (1500 °C). The lattice parameter of elementary cell decreases from a=1.0763 nm for the composition 8 mol. % ZrO$_2$-92 mol. % Gd$_2$O$_3$ to a= 1.0725 nm for the composition, containing 25 mol. % ZrO$_2$-75 mol. % Gd$_2$O$_3$ (Table. 1.12). The solid solutions based on cubic C- and monoclinic B- forms of Gd$_2$O$_3$ are separated by two phase field (B+C) which continues from 92 to 99 mol. % Gd$_2$O$_3$.
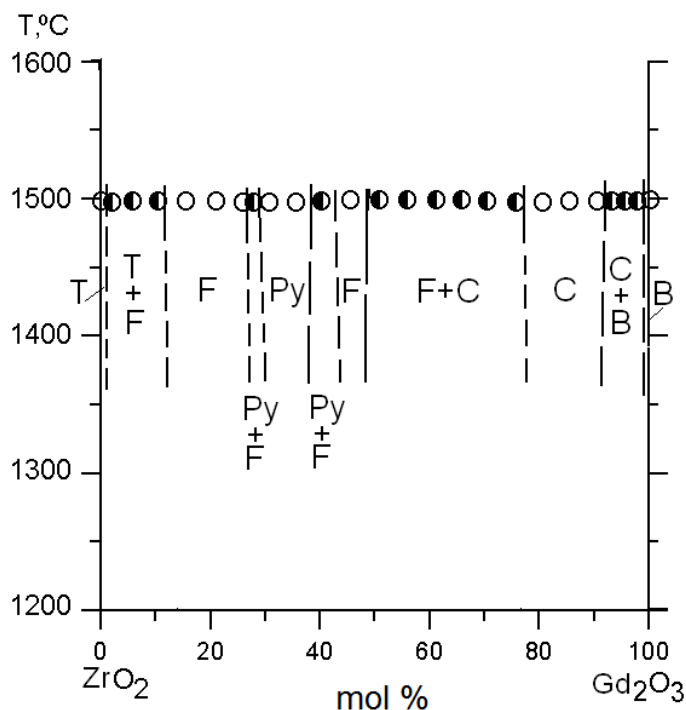

Fig. 1.22 Phase equilibria in the system ZrO$_2$-Gd$_2$O$_3$ at 1500 °C
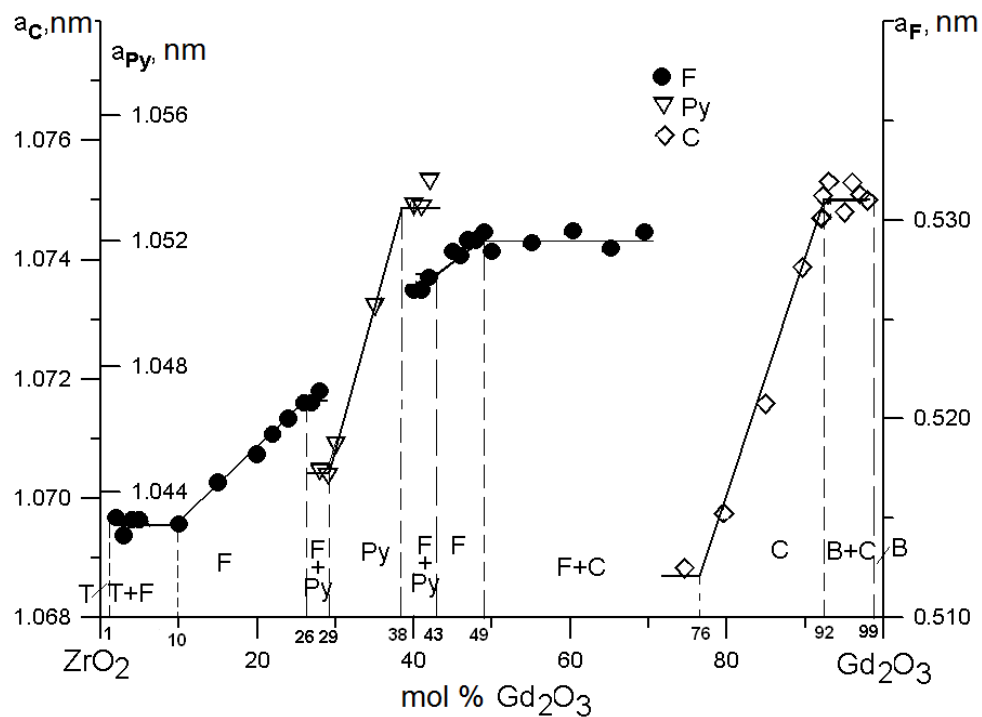(○ – one phase, ◑ - two-phase).

Fig. 1.23 Concentration dependences of the lattice parameters for solid solutions of the fluorite type (F, ●), cubic solutions of C- Gd_2O_3 (C, ◇) and cubic pyrochlore type $Gd_2Zr_2O_7$ (Py, ▽) in the system ZrO_2-Gd_2O_3 after annealing the samples at 1500 °C.

Table 1.12 Phase compositions and lattice parameters of the phases in the ZrO_2-Gd_2O_3 system after annealing at 1500 °C, 150 year (XRD data)

Chemical composition, mol. %		Phase composition and Elementary cell parameters, nm	Cell parameters for various phases, nm ($a \pm 0.0002$)		
ZrO_2	Gd_2O_3		\<C\>	\<F\>	Py
			A	a	a
1	2	3	4	5	6
0	100	\<B\> (a=1.4061; $в$=0.3566; c=0.8760; β=100.1)	-	-	-
1	99	\<B\>bas. (a=1.4370; $в$=0.3571; c=0.8759; γ=86.0) + \<C\>tr.weak.			
2	98	\<B\>bas. (a=1.4328; $в$=0.3577; c=0.8757; γ=86.1) + \<C\>	1.0759		
3	97	\<B\>basis + \<C\>↑	-		
4	96	\<B\> (a=1.4207; $в$=0.3559; c=0.9645; γ=91.3) + \<C\>↑	1.0751		
5	95	\<B\>↓ (a=1.4218; $в$=0.3392; c=0.0.9704; γ=87.1) + \<C\>bas.↑	1.0763		
6	94	\<B\>↓↓ + \<C\>bas.↑↑	1.0748		
7	93	\<B\>↓ + \<C\>bas.	-		
8	92	\<B\>tr↓ + \<C\>bas.	1.0763		
9	91	\<C\>	1.0747		
10	90	\<C\>	1.0759	-	-
15	85	\<C\>	1.0733	-	-
20	80	\<C\>	-	-	-
25	75	\<C\>bas. + \<F\>	1.0725	05363	
30	70	\<C\>bas. + \<F\>↑	1.0685	0.5352	-
35	65	\<C\> + \<F\>	1.0698	0.5306	
40	60	\<C\>↓ + \<F\>↑	1.0700	0.5308	-
45	55	\<C\>↓↓ + \<F\>↑↑		0.5297	-
50	50	\<F\> + \<C\>weak		0.5284	
51	49	\<F\> + \<C\>weak↓		0.5294	-
52	48	\<F\>		0.5290	
53	47	\<F\>	-	0.5291	-
54	46	\<F\>	-	0.5283	-
55	45	\<F\>		0.5285	
56	44	\<F\>		-	
57	43	\<F\>		-	
58	42	\<F\> + Py		0.5271	1.0539
59	41	\<F\> + Py		0.5265	1.0531
60	40	\<F\> + Py↑		0.5265	1.0531
65	35	Py		-	1.0499
70	30	Py		-	1.0455
71	29	Py		-	1.0416
72	28	Py + \<F\>		0.5215	1.0426
73	27	-	-	0.5208	-
74	26	\<F\>		0.5208	

75	25	<F>		0.5185	
76	24	<F>		0.5201	
77	23	<F>		0.5184	
78	22	<F>		0.5193	
79	21	<F>		0.5184	
80	20	<F>		0.5183	
85	15	<F>	-	0.5158	-
90	10	<F> + <T>*tr.	-	0.5148	-
95	5	<F> + <T>*↑	-	0.5136	-
96	4	<F> + <T>*↑ (a=0.5129; $в$=0.5235; c=0.5223; γ=81.8)	-	0.5137	-
97	3	<F>↓ + <T>*↑ (a=0.5085; $в$=0.5224; c=0.5219; γ=85.3)	-	0.5129	-
98	2	<F>↓↓ + <T>*↑↑ (a=0.5141; $в$=0.5291; c=0.5218; γ=80.9)	-	0.5137	-
99	1	<F>tr + <T>*bas. (a=0.5301; $в$=0.5221; c=0.5218; γ=88.1)	-	-	-
100	0	<T>* (a=0.5147; $в$=0.5203; c=0.5315; β=99.28)	-	-	-

Table 1.13 Phase composition and lattice parameters for the phases in the system ZrO_2-Gd_2O_3 after melting (XRD data)

Chemical composition, mol. %		Phase composition	Parameters of elementary cells, nm					
ZrO_2	Gd_2O_3		<F>	Py	<X>*			
			a	a	a	b	c	β
1	2	3	4	5	6	7	8	9
99	1	<M>+<F>weak	-	-	-	-	-	-
98	2	<M>+<F>↑	0.5125	-	-	-	-	-
95	5	<M>↓+<F>	0.5137	-	-	-	-	-
90	10	<F>+<M>weak	0.5153	-	-	-	-	-
85	15	<F>+<M>weak	0.5172	-	-	-	-	-
80	20	<F>+<M>weak	0.5184	-	-	-	-	-
75	25	<F>+Py	0.5202	-	-	-	-	-
70	30	<F>+Py↑	0.5217	-	-	-	-	-
67.5	32.5	<F>+Py↑	0.5233	-	-	-	-	-
65	35	<F>+Py	0.5233	-	-	-	-	-
62.5	37.5	<F>+Py	0.5261	1.0504	-	-	-	-
60	40	<F>+Py	0.5265		-	-	-	-
55	45	<F>+Py	0.5281		-	-	-	-
50	50	<F>+<C>	0.5303	-	-	-	-	-
45	55	<F>+<C>	0.5313	-	-	-	-	-
40	60	<F>+<C>	0.5324	-	-	-	-	-
35	65	<F>+<C>	0.5317	-	-	-	-	-
30	70	<X>*+<F>	-	-	-	-	-	-
25	75	<X>*+<F>	-	-				
20	80	<X>*+<F>	-	-				
15	85	<X>*+<F>weak	-	-				
10	90	<X>*	-	-				

5	95	<X>*	-	-				
2.5	97.5	<X>*	-	-				
0	100	<X*>	-	-	1.4409	0.357	0.8489	93.63

*) High temperature phase X-Gd$_2$O$_3$ cannot be quenched under given conditions, instead of this the B- Gd$_2$O$_3$ has been revealed instead.

* Under given conditions (T=1500 °C, 150 h., in air) the tetragonal phase of T-ZrO$_2$ cannot be fixed on quenching, the monoclinic phase has been found M-ZrO$_2$ instead.

designations: <B> – solid solutions based on monoclinic Gd$_2$O$_3$; <T> – solid solutions based on tetragonal modification of ZrO$_2$; <C> – solid solutions based on cubic form of Gd$_2$O$_3$; <F> – solid solutions based on cubic form of ZrO$_2$; Py – ordered phase Gd$_2$Zr$_2$O$_7$ of pyrochlore type. Other designations: bas. – basis phase, which is the main component of the phase mixture, weak traces – weak lines on diffraction patterns, ↑ – amount increases, ↓ – amount decreases.

The homogeneity field of <B-Gd$_2$O$_3$> is rather small. In accordance with XRD data, in the sample with 1 mol. % ZrO$_2$-99 mol. % Gd$_2$O$_3$, the traces of C phase were found. The solubility of ZrO$_2$ in the B-form of Gd$_2$O$_3$ is almost 1 mol. % (1500°C). The lattice parameters of the elementary cell of B phase varies from a=1.4061, $в$=0.3566, c=0.8760 nm, γ=100.1 in pure Gd$_2$O$_3$ to a=1.4370, $в$=0.3571, c=0.8759 nm, γ=86.0 for boundary solid solutions.

The specific microstructures corresponding to different phase fields on the diagram of the ZrO$_2$-Gd$_2$O$_3$ system at 1500 °C are presented in Fig. 1.24. At high temperatures (> 2300 °C), and high content of Gd$_2$O$_3$ the solid solutions in the systems are formed based on high-temperature cubic (X) form of gadolinia, however as a result of melting under given conditions followed by slow cooling of the samples, the X-Gd$_2$O$_3$ phase cannot be fixed with quenching, and instead of it the low temperature monoclinic (B) phase of Gd$_2$O$_3$ is formed. The specific microstructures of melted and quenched samples in the systems ZrO$_2$-Gd$_2$O$_3$, are shown in Fig. 1.25.

The melted samples containing from 67.5 to 55 mol. % ZrO$_2$ are characterized by co-existence of two phases which are distinguished by contrast. In these samples, the pyrochlore phase primary precipitations have been observed (intergrain phase) together with other phase of F- ZrO$_2$ coarse crystals. The grain size of F- ZrO$_2$ varies by length from 45.83 μm до 16.66 μm.

The microstructure of undereutectic composition containing 30 mol. % ZrO$_2$ includes grains of F-ZrO$_2$, which are represented by sintered agglomerates substantially elongated, and eutectic filled intergrain spaces. The microstructure of the overeutectic composition is presented in Fig. 1.24, 1.25 e. This sample containing 20 mol. % ZrO$_2$ includes of light matrix grains of polyhedral shape of Gd$_2$O$_3$ by the XRD data, and eutectic filled intergrain spaces.

Thus, phase equilibria if the ZrO$_2$-Gd$_2$O$_3$ system from melting temperatures to 1500 ºC were studied. For this system, formation of boundary solid solutions based on various crystalline forms of input oxide components and the pyrochlore-type phase Gd$_2$Zr$_2$O$_7$ (Py) is very specific. The results confirmed elongated phase fields, revealed in this paper, especially in the gadolinia rich part of the phase diagram: homogeneity field of solid solutions based on C-Gd$_2$O$_3$ and two phase field (C+B) at temperature 1450 °C, respectively. Study of the phase equilibria in the system at high temperatures (> 2300 °C) has shown the composition 25 mol % ZrO$_2$-75 mol % Gd$_2$O$_3$ corresponds to eutectic coordinates.
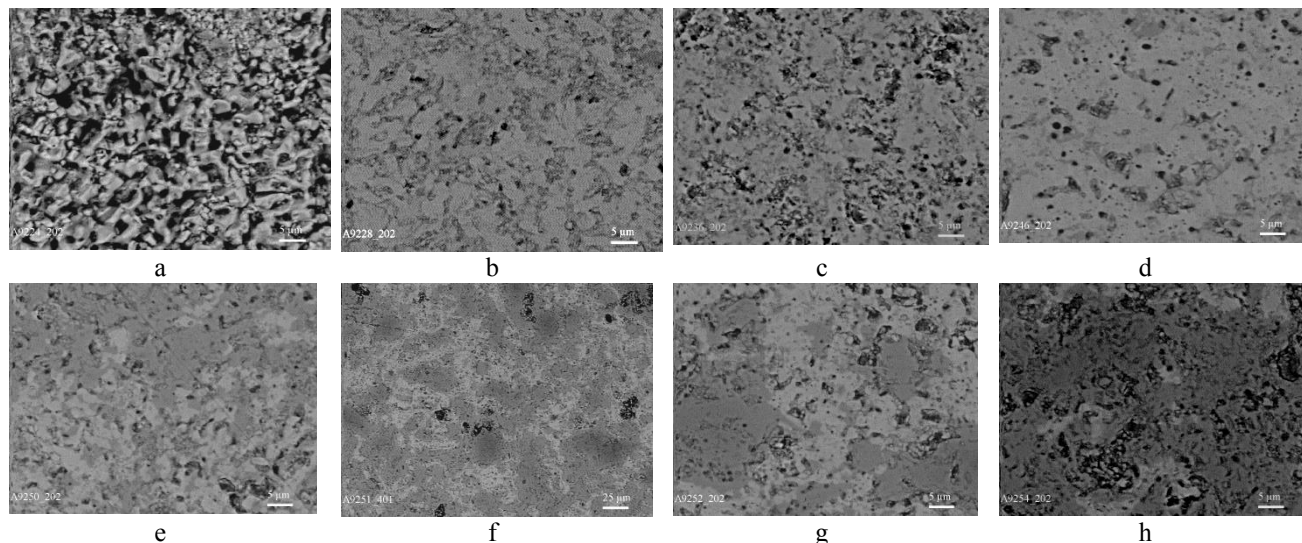
Fig. 1.24 - Microstructure of the samples in the ZrO_2-Gd_2O_3 system after annealing at 1500 °C:
a) 2 mol % ZrO_2- 98mol % Gd_2O_3, <B>bas + <C>, BEI, × 2000;
b) 4 mol % ZrO_2-96 mol % Gd_2O_3, <B> + <C>↑, BEI, × 2000;
c) 8 mol % ZrO_2-92 mol % Gd_2O_3, <B>↓ + <C>bas., BEI, × 2000;
dark phase - <C-Gd_2O_3>, light phase - < B-Gd_2O_3>, black phase – pores;
d) 25 mol % ZrO_2-75 mol % Gd_2O_3, <F> + <C>bas., BEI, × 2000;
e) 35 mol % ZrO_2-65 mol % Gd_2O_3, <F> + <C>, BEI, × 2000;
f) 40 mol % ZrO_2-60 mol % Gd_2O_3, <F>↑ + <C>↓, BEI, × 400;
g) 40 mol % ZrO_2-60 mol % Gd_2O_3, <F>↑ + <C>↓, BEI, × 2000;
h) 45 mol % ZrO_2-55 mol % Gd_2O_3, <F>bas. + <C>↓↓, BEI, × 2000;
Light phase – <C-Gd_2O_3>, dark phase - <F-ZrO_2>, a – pores.
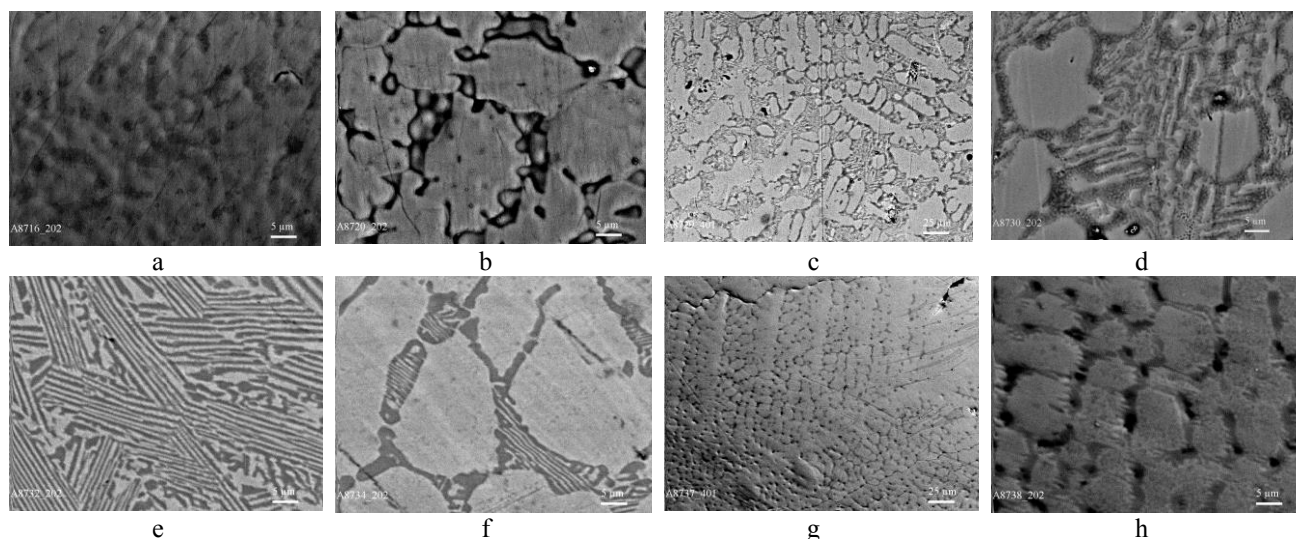
Fig. 1. 25 - Microstructure of the melted samples in the ZrO_2-Gd_2O_3 system
a) 62.5 mol % ZrO_2- 37.5mol % Gd_2O_3, <F> + Py, BEI, × 2000;
b) 55 mol % ZrO_2-45 mol % Gd_2O_3, <F> + Py, BEI, × 2000;
c) 30 mol % ZrO_2-70 mol % Gd_2O_3, <F> in eutectics, BEI, × 400;
d) 30 mol % ZrO_2-70 mol % Gd_2O_3, <F> in eutectics, BEI, × 2000;
e) 25 mol % ZrO_2-75 mol % Gd_2O_3, eutectics, BEI, × 2000;
f) 20 mol % ZrO_2-80 mol % Gd_2O_3, <Gd_2O_3> in eutectics, BEI, × 2000;
g) 15 mol % ZrO_2-85 mol % Gd_2O_3, <Gd_2O_3>, BEI, × 400;
h) 15 mol % ZrO_2-85 mol % Gd_2O_3, <Gd_2O_3>, × 2000.

1.2. The system CeO_2-Gd_2O_3

Study of the solid state reaction of CeO_2 (fluorite type, F) and Gd_2O_3 (monoclinic modification of rear earth oxides (B) at temperature 1500 °C has shown that in the CeO_2-Gd_2O_3 system three types of solid solutions are formed: cubic structure of fluorite type F-CeO_2 and C-Gd_2O_3, as well as monoclinic form of B-Gd_2O_3, which are divided by two phase fields (F+C) and (C+B), respectively (fig. 1.26). The output chemical and phase composition of the samples, annealed at 1500 °C, periods of crystalline lattices of the equilibrium phases at this temperature, are presented in Table 1.14.

The specific microstructures of the phases formed at 1500 °C in the system CeO_2-Gd_2O_3 are shown in Figs. 1.27. The boundaries of the homogeneity fields of the solid solutions based on F-CeO_2, C- and B-Gd_2O_3 were determined with the aid of compositions, containing 0-15, 65-85 and 98-100 mol % Gd_2O_3 at 1500 °C (Table. 1.14).

From the data presented, the solubility of Gd_2O_3 in F- CeO_2 achieves 15 mol % at 1500 °C. The lattice parameters increase from $a=0.5409$ nm for pure CeO_2 to $a=0.5420$ nm for the sample containing 15 mol % Gd_2O_3. The solubility of CeO_2 in monoclinic B- gadolinia is around 2 mol % CeO_2 (1500 °C). The lattice parametrs for the B phase vary from $a=1.4061$, $в=0.3566$, $c=0.8760$ nm, $\gamma=100.1$ in pure Gd_2O_3 to $a=1.4380$, $в=0.3572$, $c=0.8783$ nm, $\gamma=86.9$ in boundary solid solution. With increase of ceria concentration the lines of C-forms of Gd_2O_3 decrease on the diffraction patterns. The lattice parameters of C-phase change from $a = 1.0783$ nm in the sample with 15 mol % CeO_2-85 mol % Gd_2O_3 to $a = 1.0804$ nm in solid solution with 35 mol % CeO_2- 65 mol % Gd_2O_3. The x-ray diffraction studies were confirmed with electron microscopy data (Fig. 1.27). Specific microstructures of two phase samples (B+C) obtained at 1500 °C are presented in (Fig 1.27 c-d). Phases differ by contrast in accordance with micro-x-ray spectral analysis: light matrix phase corresponds to monoclinic B gadolinia, gray inclusions contain more ceria, i.e. belong to cubic C modification of Gd_2O_3. Determined, that with increase of ceria content B phase will become more finegraine. Light grain size of <B-Gd_2O_3> change by length from ~ 6.66-0.83 μm to 1.25-0.166 μm in the samples containing 1 mol % CeO_2-99 mol % Gd_2O_3 and 5 mol % CeO_2-95 mol % Gd_2O_3, respectively. Microstructures, specific for two phase field (C+F) at 1500 °C presented in Figs. 1.27. e-h. The sample 55 mol % CeO_2 – 45 mol % Gd_2O_3 includes two structure components. The light gray matrix C-Gd_2O_3 with dark inclusions of F- CeO_2 of non-isometric shapes and sizes 6.94-1.38 μm.
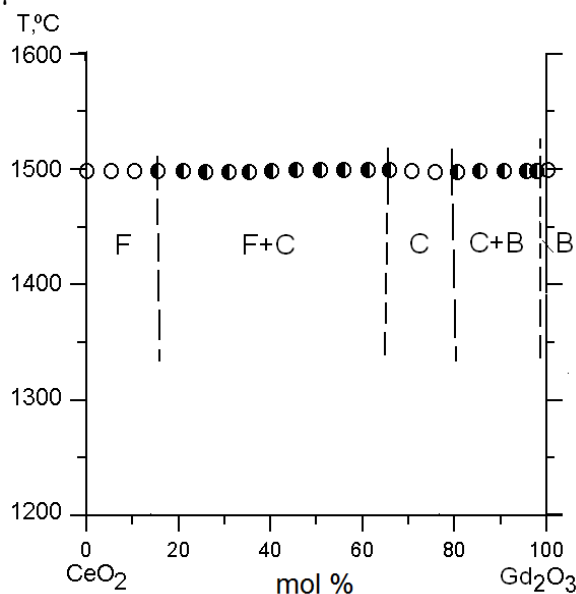
Fig. 1.26. Phase equilibrium in the system CeO_2-Gd_2O_3 at 1500 °C
(○ – one phase, ◑ - two phase samples).
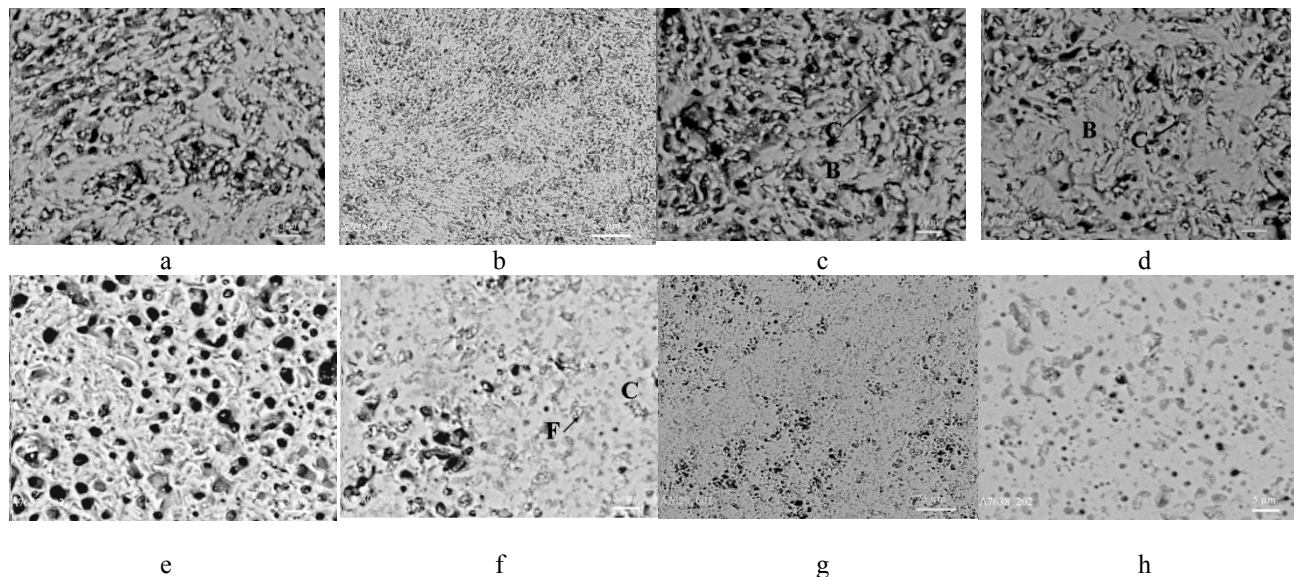
Figs. 1. 27. Microstructures in the system CeO_2-Gd_2O_3 at 1500 °C:
a) 1 mol % CeO_2 - 99 mol % Gd_2O_3, B-Gd_2O_3 bas., BEI, × 2000;
b) 1 mol % CeO_2 – 99 mol % Gd_2O_3, B-Gd_2O_3 bas., BEI, × 600;
c) 2 mol % CeO_2 – 98 mol % Gd_2O_3, B-Gd_2O_3 + C-Gd_2O_3, BEI, × 2000;
d) 5 mol % CeO_2 - 95 mol % Gd_2O_3, B-Gd_2O_3+ C-Gd_2O_3, BEI, × 2000;
light matrix - <B-Gd_2O_3>, gray inclusions - <C- Gd_2O_3>, black – pores;
e) 35 mol % CeO_2 - 65 mol % Gd_2O_3, C-Gd_2O_3 + F-CeO_2, BEI, × 2000;
f) 35 mol % CeO_2 - 65 mol % Gd_2O_3, C-Gd_2O_3 + F-CeO_2, BEI, × 600;
g) 45 mol % CeO_2 - 55 mol % Gd_2O_3, C-Gd_2O_3+F-CeO_2, BEI, × 2000;
h) 55 mol % CeO_2 - 45 mol % Gd_2O_3, C-Gd_2O_3 + F-CeO_2 , BEI, × 600;
i) 90 mol % CeO_2 – 10 mol % Gd_2O_3, F-CeO_2, BEI, × 2000;
j) 90 mol % CeO_2 – 10 mol % Gd_2O_3, F-CeO_2, BEI, × 600,
light matrix - <C-Gd_2O_3>, gray inclusions - <F- CeO_2>, black – pores.

Table 1.14 Phase compositions and lattice parameters of the phases after annealing in the CeO_2-Gd_2O_3 system at 1500 °C, for 150 h. (XRD data)

Chemical composition, mol %		Phase composition	Lattice parameters, nm ($a \pm 0.0002$)					
			<F>	<C>	<B>			
CeO_2	Gd_2O_3		a	a	a	B	c	β
1	2	3	4	5	6	7		
0	100	<B>	-	-	1.4061	0.3566	0.8760	100.1
1	99	<B>bas.	-	-	1.6026	0.3568	0.8825	96.0
2	98	<B>bas. + <C>weak	-	-	1.4380	0.3572	0.8783	86.9
3	97	<B> + <C>tr.↑	-	1.0807	1.4276	0.3472	1.0628	87.7
4	96	<B> + <C>↑	-	1.0804	1.4211	0.3472	1.0755	91.3
5	95	<B>↓ + <C>↑	-	-	1.4212	0.3466	1.0742	87.2.
10	90	<B>↓ + <C>↑	-	1.0804	1.3905	0.3392	0.9566	83.8
15	85	<B>↓ + <C>bas.	-	1.0783	-	-	-	-
20	80	<C>bas.	-	1.0813	-	-	-	-
25	75	<C>	-	1.0785	-	-	-	-
30	70	<C>	-	1.0805	-	-	-	-
35	65	<C> + <F>	0.5403	1.0804	-	-	-	-
40	60	<C> + <F>	0.5402	1.0804	-	-	-	-
45	55	<C> + <F>	0.5406	1.0811	-	-	-	-
50	50	<C> + <F>	0.5403	1.0805	-	-	-	-
55	45	<C> + <F>	0.5409	1.0812	-	-	-	-
60	40	<C>↓ + <F>	0.5420	1.0831	-	-	-	-
65	35	<C>↓ + <F>bas.	0.5416	-	-	-	-	-
70	30	<C>tr.↓ + <F>bas.	0.5420	-	-	-	-	-
75	25	<F>bas. + <C>weak.↓↓	0.5414	-	-	-	-	-
80	20	<F>bas. + <C>weak.↓↓	0.5420	-	-	-	-	-
85	15	<F> + <C>tr.	0.5420	-	-	-	-	-
90	10	<F>	0.5423	-	-	-	-	-
95	5	<F>	0.5410	-	-	-	-	-
100	0	<F>	0.5409	-	-	-	-	-

Marking: <B> is a solid solution based on monoclinic Gd_2O_3; <C> is a solid solution based on cubic rare earth oxides such as Gd_2O_3; <F> is a solid solution based on cubic phase CeO_2 of fluorite type. Other symbols: bas. is the main phase, weak means low intensity peaks, tr. means traces of the phase, ↑ means increasing of the phase amount, ↓ means decreasing of the phase amount.

2. Transparent ceramics manufacturing

Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG, cubic) ceramics doped with luminescent centers of rare earth ions (RE^{3+}), such as Nd^{3+} and Yb^{3+}, are well studied materials for high-power laser applications because of their high quantum efficiency and high enough mechanical and thermal properties. Recently, operation of a 100 kW JHPSSL Nd:YAG laser was demonstrated using high purity ceramics materials [1]. Alternatively to cubic garnets, the transparent ceramic matrices based on rare earth oxides and their compounds are considered perspective for advanced laser systems. Pure rare-earth oxides of yttria sub-group or their solid solutions with cubic symmetry of lattice (C-type REO) and, therefore, arbitrarily oriented grains in ceramics are widely studied. For instance, solid solutions based on Y_2O_3-La_2O_3 system (such as $La_xY_{2-x}O_3$, where x=0.05÷0.20) doped with scintillating additives (Nd, Eu, Sm, Tb, Er, Yb) have been subject of research. Many excellent characteristics were achieved for these laser media, but all of them did not result in breakthrough properties as compared to ones of garnets.

Besides high symmetry cubic crystals, the non-cubic anisotropic crystals attract interest to be more effective laser matrices than their isotropic competitors because they enable to harvest excitation energy from two directions of irradiations, but emit monochromatically mostly in one selected direction. The fabrication of laser-grade anisotropic ceramics through the conventional particulate processes is not realistic because of resulting randomly oriented grains and grain boundaries and, therefore, additional optical scattering. Fabrication of transparent polycrystalline ceramics from non-cubic materials requires precise crystal orientation control so that optical scattering losses at the grain boundaries are prevented [2]. The manufacturing of transparent anisotropic ceramics by using a new crystal orientation process of particles deposition in strong magnetic field (DSMF) is grounded on the property of large magnetic anisotropy induced by 4f electrons of RE^{3+} ions (scheme in Fig. 2.1). In the case of ideal alinement of anisotropic grains strictly along one axis, the DSMF offers a key approach to extremely high-power laser materials such as RE:FAP and patterning process for multi-function integrated monolithic solid-state lasers [3]. For example, they have first proposed realization of transparent anisotropic laser ceramics by using a new crystal orientation process based on large magnetic anisotropy induced by 4f electrons of rare earth oxides. Applying the slip casting in a 1,4 T magnetic field followed by heat treatment, there have been successfully fabricated laser-grade rare-earth-doped calcium fluorapatite ceramics with a loss coefficient of 1,5 cm^{-1} [2].
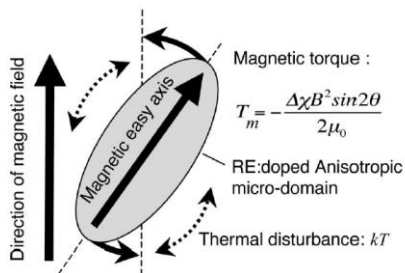
Fig. 2.1. Schematic of the RE-assisted magnetic orientation method for fabrication of RE-doped anisotropic laser ceramics. The magnetic anisotropy $\Delta\chi$ is enhanced by RE doping [$\Delta\chi = 10^{-4} - 10^{-6}$ (RE doped), $\Delta\chi = 10^{-6} - 10^{-7}$ (undoped)] [2].

From the literature review we have learned the main requirements to *rare-earth-doped anisotropic ceramic materials* can be formulated as follows:
- *large stimulated emission;*
- *big absorption cross sections;*
- *long fluorescence life time [4];*
- *high quantum efficiency;*
- *excellent optical characteristics: superior transparency higher than 80%;*
- *superior mechanical and thermo-mechanical properties;*

- *fabrication of transparent polycrystalline ceramics from non-cubic materials requires precise crystal orientation control so that;*
- *optical scattering losses at the grain boundaries are prevented;*
- *crystal orientation of diamagnetic and paramagnetic materials, as well as that of magnetic materials, can be controlled by imposing a high magnetic field of 1÷10 T [5-8] as dependent on magnetic susceptibility difference.*

For instance, the $Sr_5(PO_4)_3F$, has been chosen as host material, due to its favorable spectroscopic properties such as high emission and absorption cross-sections, large induced crystal field splitting. In $Sr_5(PO_4)_3F$ lattice, two inequivalent cation sites are present: $Sr(1)$ with C_s symmetry is surrounded by six oxygen atoms and one fluorine atom, whereas the $Sr(2)$ with C_3 symmetry is coordinated to nine oxygen. Among lanthanides ions, it is well known that Eu^{3+} is suitable as a probe for determination of local structure in the host matrix because of their simple multiplet pattern and straight forward symmetry behavior of the energy levels. RE^{3+} can substitute for Sr^{2+} ions at both sites in terms of the similar radius of them. Generally, the substitution of RE^{3+} for Sr^{2+} ions depends on the local charge compensation.

In the framework of present project, it has been supposed that the materials based on orthorhombic phase of $LaYO_3$ type doped with scintillating additives (Nd_2O_3, Yb_2O_3) is prospective for research. The crystal structure of $LaYO_3$ ($LaYbO_3$) ceramics have been investigated by Rietveld refinements performed on X-ray data. They showed the room-temperature structure to be best described by the orthorhombic Pnma space group [a = 0.5894 nm, b = 0.6092 nm, c = 0.8496 nm, α = 90 °, β = 90 °, γ = 90 ° unit volume of 0.30506 nm^3, Z4, and theoretical density, $D(LaYO_3)$=6.01 g/cm^3, $D(LaYbO_3)$=8.04 g/cm^3] in agreement with electron diffraction experiments. $LaYO_3$ perovskite demonstrates difference in magnetic susceptibility similar to its crystallography analog of $LaYbO_3$ of $(2÷5)*10^{-6}$. Such a value of magnetic anisotropy appears to be enough for dipole's orientation in suspension under strong magnetic field of 1-10 T.

Properties of the samarium doped $LaYO_3$ nanocrystalline phosphor powders were studied in [9]. The ceramic matrix has been obtained by polymer complex solution method. Crystallization from the amorphous state (with some residuals of carbon) resulted in nanoparticles with crystalline structure corresponding to distorted perovskite type structure for the first time. Luminescence properties of Sm^{3+} doped $LaYO_3$ particles exhibited characteristic orange-to-red emission coming from the intra-4f-shell 4G5/2 →6HJ electron transitions with emission decay of 1.5 ms. Energy level positions are derived from emission and excitation spectra [9].

Ceramics fired at 1600 °C for 4 h attain ~97% of theoretical density and their microstructures consist of randomly distributed equiaxed grains with an average size of ~8 μm. Conventional transmission electron microscopy shows densification to occur in the absence of a liquid phase and reveals domain-free grains. Conductivity measurements show that the doped-$LaYO_3$ is a *p*-type semiconductor at high oxygen partial pressures, but becomes a pure oxide-ion conductor at low oxygen partial pressures [10], which is good to define sintering medium.

The fabrication of textured ceramics has been carefully developed recently, due to a growing necessity of manufacturing advanced ceramics materials that have to meet definite requirements concerning their properties. A controlled development of crystalline texture in ceramics makes it feasible to improve some optical, electrical, piezoelectric and mechanical properties of those materials. There are few methods of producing textured ceramics elaborated so far, including template grain grow (TGG) or hot forging. Magnetic alignment is one of the most recent and well researched method [5]. The idea is to make the ceramic particles in a suspension aligned during the colloidal processing due to the influence of a high magnetic field. The strong texture can be developed during subsequent sintering of the shaped elements. The shaping itself is conducted usually by slip casting. This way of fabricating textured ceramics is becoming popular because it does not require large templates or high uniaxial pressure. α-Alumina, commonly used in ceramics processing, belongs to the rhombohedral crystalline system. It exhibits anisotropic susceptibility, but this anisotropy had been more or less ignored due to its very low value. The development of

superconducting magnet has extended the potential applications of strong magnetic fields for particle alinement.

2.1 Synthesis of nanosize powders

The sub-project is about manufacturing of optically transparent polycrystalline ceramic materials based on high-melting oxides such as isotropic yttria-alumina garnet ($Nd:Y_3Al_5O_{12}$) and anisotropic $RE:LaYO_3$ (RE = Nd, Yb). This part includes: synthesis of nanosize powders for various solid solutions based on $LaYO_3$ and $Y_3Al_5O_{12}$ in the particle size range 10-15 nm valid for manufacturing dense nanocrystalline ceramics. Note that the sub-micron in size and near-spherical particles in shape are good for dense transparent isotropic ceramics such as $Y_3Al_5O_{12}$, but for anisotropic one such as $LaYO_3$, the nanopowders of 10 nm are principal to get high transparency.

The literature search and review of the papers describing optically transparent ceramics has been carried out. More than 1000 papers and abstracts for last 20 years have been collected and reviewed, to understand the main technical approaches to achieve highly transparent ceramics of laser application. The main conclusions done are as follows:

- The Nd:YAG ceramic laser rods show currently comparable or even better emission characteristics than the similar (size, doping concentration) single crystal rods.
- Fabrication of high transparency ceramics requires 100% density to form a pore-free microstructure.
- The densification of ceramics is determined by the microstructure of the green body (such as the grain size and morphology, particle size distribution (PSD), the average size of agglomerate and pore), rather than individual particles.
- A well sinterable powder with a small particle size, narrow PSD, and low-agglomeration, is crucial for the fabrication of $RE:LaYO_3$ (RE = Nd, Yb) or Nd:YAG transparent ceramics.
- The co-precipitation is the most effective route to synthesize $Nd:Y_2O_3$ powders and others.

Synthesis of $RE:LaYO_3$ (RE = Nd, Yb) or Nd:YAG nanopowders has been carried out by the hydroxide co-precipitation method. Powders of La_2O_3, 99.99%, Y_2O_3, 99.99%, Nd_2O_3, 99.99%, Yb_2O_3, 99.99% and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 1N HNO_3 solution, respectively. These solutions were mixed at the stoichiometric ratio to form the Nd:YAG, $Nd:LaYO_3$ or $Yb:LaYO_3$ precursors. The solution was stirred under ultrasonic irradiation. Co-precipitation of rare earth hydroxides was carried out in the reactor with permanent stirring by dropping of 0.1 N solution to cold ammonia solutions (ammonium hydrocarbonate, sulphate). For complete precipitation the pH was maintained near 9. The precipitates were dried through several steps: the mixed precipitate was dried in a vacuum drying chamber at 80 °C for 24 h to remove the main portion of crystalline water, and then temperature was raised to 200 °C for 3 h to remove the rest of crystalline water. Final firing has been done at 600 °C for 2-3 hours until complete crystallization of precipitate. Firing to get high degree of crystallinity of particles has been done above 1200 °C for 2-20 hours. This heat treatment is especially important to get particles orientable in strong magnetic field. After annealing the powders were grinded manually in mortar followed by homogenizing in Teflon ball mill charged with zirconia 3 mm balls in the media of absolute alcohol with additives of polyethyleneimine solution. The nanopowders of neodymia (ytterbia) doped $LaYO_3$ were characterized in their properties using: specific surface area measurements (BET and BJH methods, by ASAP 2000), particle size distribution by laser granulometry (Malvern Nanosizer), particle shape and structure by electron microscopy. Stoichiometry and concentration of luminescent dopants (neodymia, and ytterbia) has been determined by x-ray fluorescent method using Rigaku Primini spectrometer. Full technological scheme from chemicals to sintered ceramics is presented in fig. 2.2.
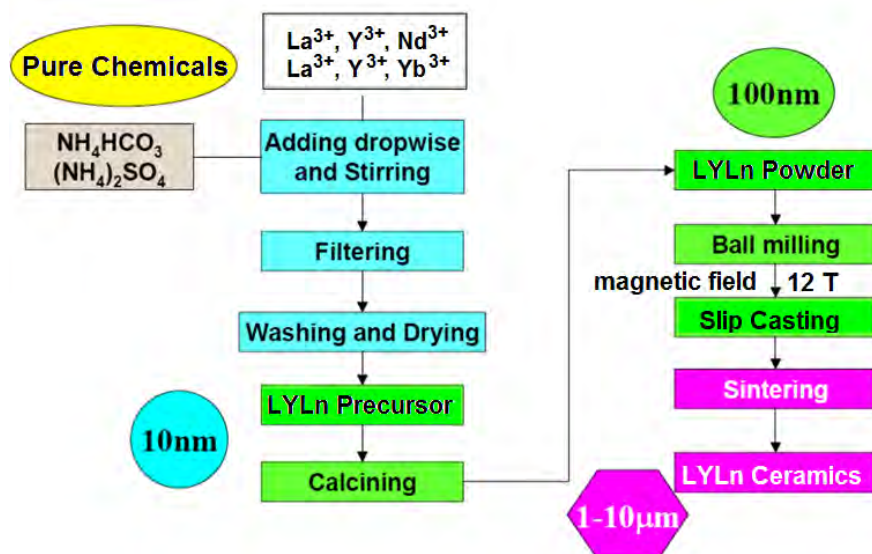
Fig. 2.2 Technological scheme for manufacturing of transparent ceramics

Characterization of Nd:Y_2O_3 nanopowders.

The precipitates of Nd:Y_2O_3 after drying and water removal were XRD-amorphous. The specific surface area was about 60 ±5 m^2/g independently on concentration of neodymium. The particle size distribution measuring has shown mean particle size of 15-20 nm and agglomerate sizes increasing from 35 to 70 nm. The transmission electron microscopy data has shown the Nd:Y_2O_3 nanoparticles are almost spherical in shape, weakly agglomerated (Table 2.1).

Table 2.1 Characteristics of particulate samples based on Nd:Y_2O_3.

Powder sample #	Content of Nd at %	Specific surface area, m^2/g	Mean particle size, nm	Agglomerate size, nm	Time of de-agglomeration, hour
Y001	0.06	58.2	18	37	24
Y002	0.1	55.8	20	48	24
Y003	0.2	59.4	18	45	24
Y004	0.6	62.3	16	53	24
Y005	1.0	60.7	15	45	36
Y006	1.2	59.6	18	59	36
Y007	1.4	64.4	15	66	48
Y008	1.6	61.9	16	72	48

agglomerates

particles

Microscopy image of Nd:Y_2O_3 nanoparticles

Fig. 2.3 Examples of the particle size distributions (agglomerates and true particles) and their view.

Particle size distribution has been controlled by Malvern ZetaSizer and shown mean particle size range 10-22 nm assembled to agglomerates of 40-120 nm in size. Agglomeration was found to depend on drying conditions. To get homogeneous suspensions, durable grinding has been provided for 24-48 hours in alcohol medium. Powders were mixed with 0.5 wt.% tetraethyl orthosilicate (TEOS) added as sintering aid. Preliminary pressed at 100-380 MPa samples were subjected to hydrostatic compression at 200-500 MPa. The best green density of 56% theoretical has been achieved.

Table 2.2. Characteristics of particulate samples based on Nd:YAG

Powder sample #	Content of Nd at %	Specific surface area, m^2/g	Mean particle size, nm	Agglomerate size, nm	Time of de-agglomeration, hour
YAG001	0.06	93	14	44	24
YAG002	0.1	85	15	53	24
YAG003	0.2	103	11	51	24
YAG004	0.6	88	15	49	24
YAG005	1.0	77	17	66	48
YAG006	1.1	73	19	73	48
YAG007	1.2	74,5	17	79	48
YAG008	1.3	62	22	87	48

Characterization of Ln:LaYO₃ nanopowders.

The precipitates of Ln:LaYO$_3$ after drying and water removal were XRD-amorphous. The specific surface area was about $80 \div 110 \pm 5$ m^2/g independently on concentration of dopant for all dopants used. The particle size distribution measured for 1.0-10 at.% doped perovskites has shown mean particle size of 10-20 nm and agglomerate sizes increasing from 45 to 170 nm. The results of laser granulometry are presented in Fig. 2.4 (a-c). The field emission scanning electron microscopy data has shown the Nd:LaYO$_3$ nanoparticles are almost spherical in shape, and agglomerated (Fig. 2.5).
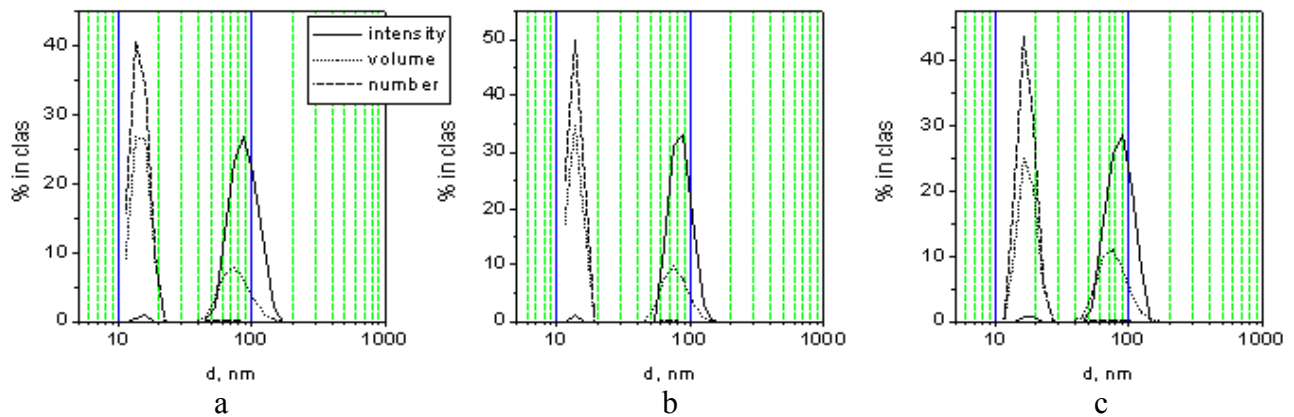
Fig. 2.4 Particle size distribution of the Nd:LaYO$_3$ (a), Eu:LaYO$_3$ (b), Yb:LaYO$_3$ (c).

Annealing of as-prepared powders has been carried out at 1200 °C for 10-20 hours to allow amorphous particles to be crystallized and growth by coalescence. Before using slip casting in magnetic field, the particles must be stable, single crystalline and easy for suspending. The typical XRD pattern of Nd:LaYO$_3$ is presented in Fig. 2.6. To get homogeneous suspensions, durable grinding has been provided for 24-48 hours in alcohol medium in fluoroplastic drum with zirconia balls. The as-annealed powders of Nd:LaYO$_3$ with average particle size of 220 nm is shown in Fig. 2.7.
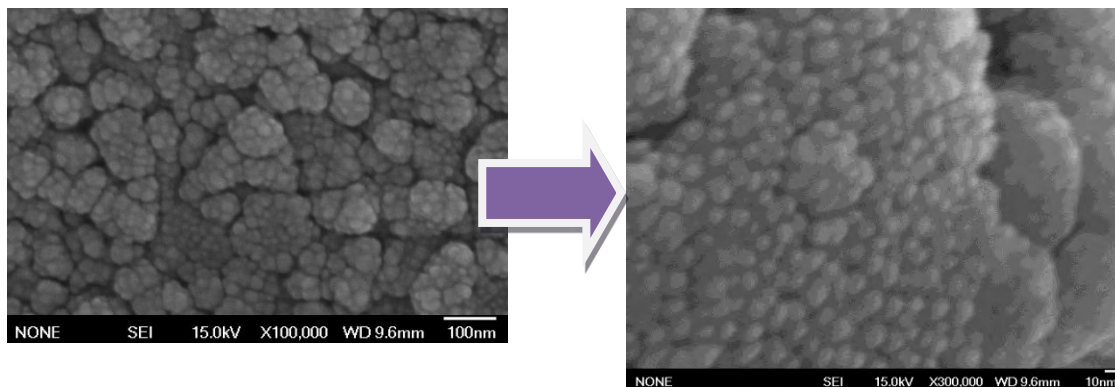
Fig. 2.5. Agglomerates of the Nd:LaYO$_3$ nanoparticles and internal structure of agglomerates with particle sizes of 10-20 nm assembled in agglomerates of 100-170 nm size.

Table 2.3 Characteristics of particulate samples based on Ln:LaYO$_3$.

Powder sample #	Content of Ln at %	Specific surface area, m^2/g	Mean particle size, nm	Agglomerate size, nm	Regime of annealing °C / hours	Time of de-agglomeration, hour
Nd:LaYO$_3$						
Nd001	1.0	85.8	12	77	1200 / 10	48
Nd002	3	69.1	15	83	1200 / 10	48
Nd003	5	59.4	18	89	1200 / 10	48
Nd004	10	48.3	21	103	1200 / 10	48
Yb:LaYO$_3$						
Yb001	1.0	60.7	13	95	1200 / 20	48
Yb002	3	59.6	13	91	1200 / 20	48
Yb003	5	54.4	16	94	1200 / 20	48
Yb004	10	51.9	17	108	1200 / 20	48
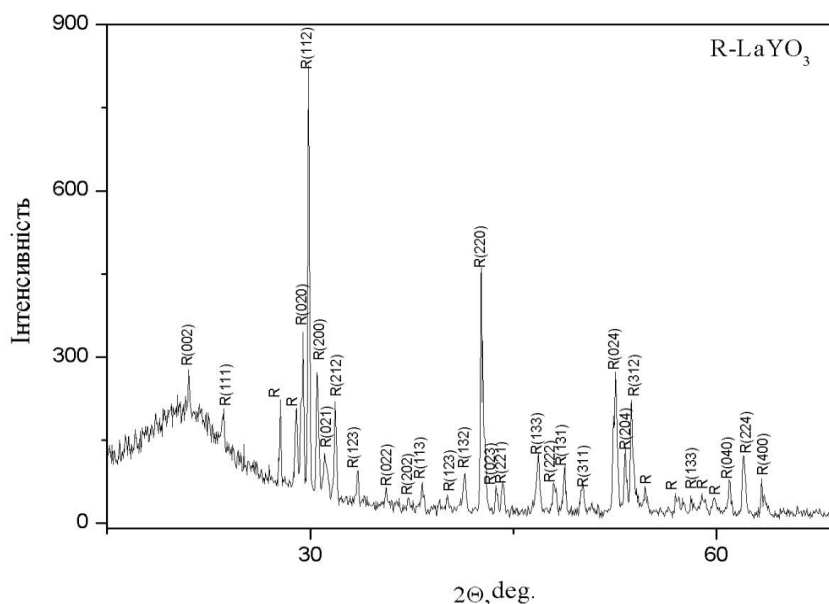
Fig. 2.6. XRD pattern of the composition 49.5% La$_2$O$_3$-49.5%Y$_2$O$_3$-1%Nd$_2$O$_3$

Size(nm)	Intensity	Volume	Number
152.0	0.0	11.0	16.2
191.4	50.3	32.0	39.7
240.9	41.6	35.0	32.3
303.3	8.2	18.0	10.3
381.9	0.0	4.0	1.5
480.9	0.0	0.0	0.0
605.4	0.0	0.0	0.0
762.3	0.0	0.0	0.0
959.8	0.0	0.0	0.0
1208.4	0.0	0.0	0.0
1521.5	0.0	0.0	0.0
1915.6	0.0	0.0	0.0
2411.9	0.0	0.0	
3036.7	0.0	0.0	
3823.4	0.0	0.0	
4813.9	0.0	0.0	
6061.0	0.0	0.0	
7631.2	0.0	0.0	
9608.1	0.0	0.0	
12097.2	0.0	0.0	
15231.2	0.0	0.0	
19177.0	0.0	0.0	
24145.1	0.0	0.0	
30400.1	0.0	0.0	

Peak Analysis by intensity

Peak	Area	Mean	Width
1	100.0	221.1	99.9

Peak Analysis by volume

Peak	Area	Mean	Width
1	100.0	232.2	142.2

Peak Analysis by number

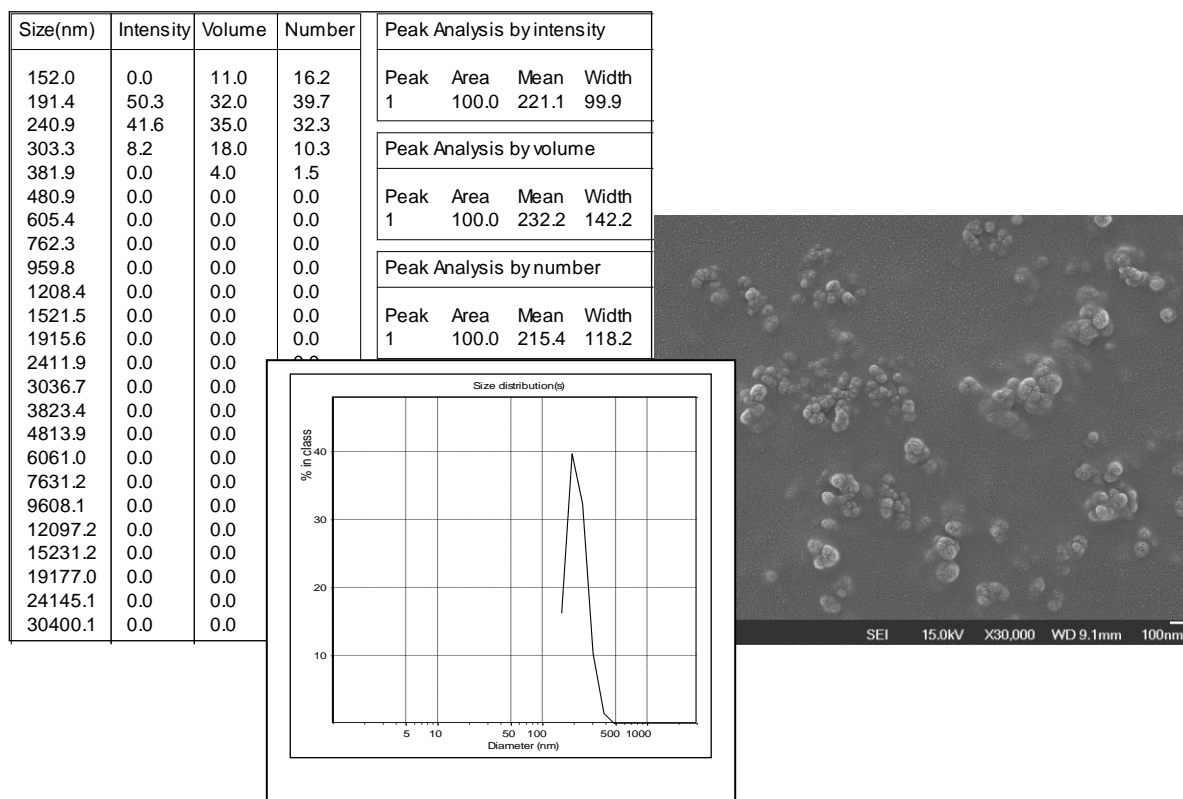| Peak	Area	Mean	Width
1	100.0	215.4	118.2

Fig. 2.7 Particle size distribution and FESEM image of as-annealed particles of Nd:LaYO$_3$.

Initially, a slurry containing Nd:LaYO$_3$ particles and absolute ethanol was mixed with a small amount of plyethyleneimine (ALON A-6114; Toaghosei Co., Tokyo, Japan) as the dispersant. (MW = 10 000 g mol−1, Wako Pure Chemical Industries, Ltd., Tokyo, Japan). The resulting mixture was mechanically ground in ball mill with zirconia balls for 48 hours to convert the aggregated particles to single particles. The suspensions of 5 vol.% solid phase loading were ultrasonically dispersed (GSD600AT; Sonic Technology Co., Ltd., Saitama, Japan) for 10 min before slip casting. The suspensions were outgassed in a vacuum to remove as many air bubbles as possible. The slurry was then poured into a porous mold, and slip casting was carried out in a horizontal static magnetic field of 12 T (JMTD-12T100NC5; Japan Superconductor Tech. Inc., Hyogo, Japan) at room temperature for 12 hours.

Green sampling.

Green density of consolidated ceramics is one of the key parameter to successfully prepare transparent ceramics on sintering. High density green samples in the range of 68-70% of theoretical density have been prepared using tape casting. In the Table 2.3 one can find data concerning wet consolidation of tapes from suspensions. The 120 nm size granules containing ceramic nanoparticles, SAR and polyvinylbuteral form densely packed samples. This density remains almost unchanged after burning out the binder and SAR. Annealing at 450 C resulted in samples ready for sintering. Green square samples of 1x1 cm were cut from the green tape. To develop the rate controlled sintering regime for optical ceramic, the preliminary sintering experiments have been started and are in progress now. For each composition of Nd:Y$_2$O$_3$ and Nd:Y$_3$Al$_5$O$_{12}$ phases, from 10 to 12 various constant heating rate regimes without isothermal holding have been recorded up to 1700 °C. The isothermal hold of 2 to 12 hours has been provided then. The relative density for sintered squares is listed in the last column of the Table 2.4.

Table 2.4 Characteristics of sintered samples based on Nd:YAG

Powder sample #	Content of Nd at %	Green density, % of theor.	Sintering temperature, °C	Sintering time, Hours	Sintered density, % of theor.
YAG001	0.06	60.1 64.8 68.9	1700	2/12	96.7/98.1 97.3/98.8 98.2/99.1
YAG002	0.1	59.2 64.3 69.1	1700	2/12	96.1/98.4 97.9/99.0 98.6/99.3
YAG003	0.2	59.5 65.2 69.0	1700	2/12	95.9/97.8 96.8/98.2 98.0/98.9
YAG004	0.6	59.4 65.0 69.3	1700	2/12	96.5/98.9 97.3/99.0 98.5/99.4
YAG005	1.0	58.8 64.9 68.9	1700	2/12	96.1/97.9 97.1/98.6 98.2/99.1
YAG006	1.1	59.0 64.7 69.1	1700	2/12	96.0/97.4 96.8/98.3 98.1/99.2
YAG007	1.2	60.1 64.6 69.2	1700	2/12	95.7/97.1 96.6/98.7 97.8/99.0
YAG008	1.3	59.5 64.8 69.7	1700	2/12	95.7/97.3 97.0/98.4 98.5/99.3

The best density of the sintered ceramics of 99.0-99.4 was achieved for neodymia-doped yttria. The samples were 45-50% transparent. The garnet samples showed residual porosity (0.5-0.7%). The isothermal holds of 2-12 hours are proposed to be used at 1700 C and less to allow samples to hill the residual porosity and get transparency.

The green samples of $Nd:LaYO_3$ or $Yb:LaYO_3$ were prepared by slip casting in strong magnetic field followed by hydrostatic compression at 50 MPa to achieve uniform porosity distribution and higher density. After slip casting, the samples were dried slowly and annealed at 600 °C for 10 hours to remove organic compounds. Preliminary sintering to fix textured structure was carried out at 1200 °C.

Fully dense ceramic pieces based on rare earths can be obtained by two-step sintering and rate controlled sintering techniques. To develop the rate controlled sintering regime for optical ceramic, the kinetic field of responses for sintering experiments have been calculated. For each composition of $Nd:LaYO_3$, $Yb:LaYO_3$ phases, from 10 to 12 various constant heating rate regimes without isothermal holding have been recorded up to 1600-1700 °C. The isothermal hold of several hours has been provided if porosity higher than 1% remained after RCS mode. The relative density for sintered samples is listed in the last column of the Table 2.5.
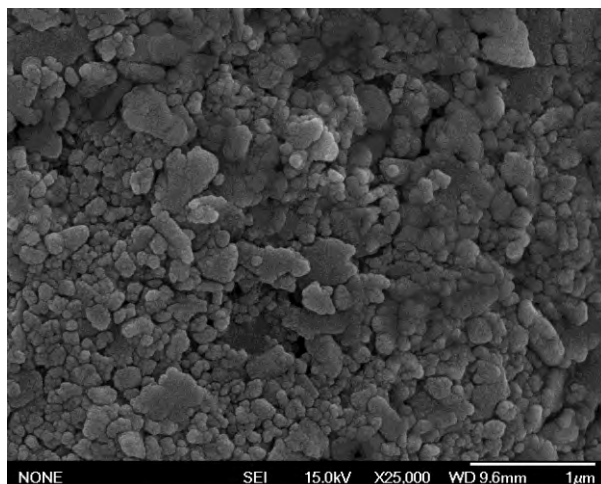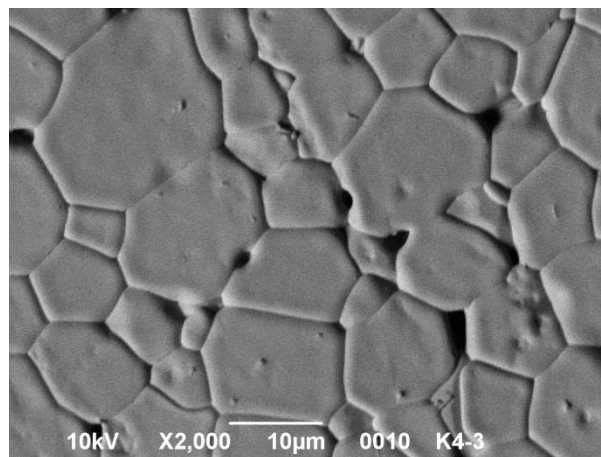
Fig. 2.8 SEM structure of green ceramics.

Fig. 2.9 SEM image of thermally etched sintered Nd:LaYO$_3$ ceramics (density 98.5%)

Table 2.5. Characteristics of sintered samples based on Ln:LaYO$_3$

Powder sample #	Content of Ln at %	Green density, % of theor.	Cold consolidation mode	Sintering regime, °C or RCS	Transparency of ceramics %	Sintered density, % of theor.
Nd001	1.0	60.1	SC+SMF + CIP	1500 air RCS	55 opaque	98.70 99.61
Nd002	3	59.2	SC+SMF + CIP	1500 air RCS	<50 opaque	98.81 99.48
Nd003	5	58.5	SC+SMF + CIP	1500 air RCS	<50 opaque	97.90 99.18
Nd004	10	59.4	SC+SMF + CIP	1500 air RCS	<55 opaque	96.55 98.97
Yb001	1.0	65.1	CIP SC+SMF + CIP	1500 air RCS	opaque ~45	98.72 99.51
Yb002	3	65.9	CIP	1500 air RCS	opaque <40	98.13 99.47
Yb003	5	64.5	CIP	1500 air RCS	opaque ~45	98.91 99.83
Yb004	10	65.4	CIP	1500 air RCS	opaque ~45	98.50 99.92

CIP – cold isostatic pressing, RCS - rate controlled sintering, SC – slip casting, SMF – strong magnetic field.

Discussion of sintering results.

Samples of all compositions (Table 2.5) were sintered above 1580 °C, i.e. 20 °C higher than decomposition point for pure LaYO$_3$. Here we supposed that the dopants increase the decomposition temeratures for the perovskite phases. The Nd$_2$O$_3$ and Yb$_2$O$_3$ dopants substitute in the lattice of LaYO$_3$ three-valent ions of La^{3+} and Y^{3+}. Following phase diagram research, the homogeneity field of R phase is directed to the Nd$_2$O$_3$ corner of the diagram of the La$_2$O$_3$-Y$_2$O$_3$-Nd$_2$O$_3$ system, respectively. This means that the ionic substitution in the sites A and B occurs

equally. In the La_2O_3-Y_2O_3-Yb_2O_3 system, ions of Yb^{3+} substitute Y^{3+} ions in the B site only. It has been revieled that the phase $Nd:LaYO_3$ is not stable at 1600 C: the mixture of other phases than $Nd:LaYO_3$ has been found. By the stability reasons for textured structure of R phase, the sintering temperature of the $Nd:LaYO_3$ should not exceed 1500-1530 °C. Unfortunately, this temperature is not enough to get fully dense transparent ceramics even starting from nanosize powders and applying different oxygen partial pressures. In the case of the phase $Yb:LaYO_3$, the sintering temperature can be much higher than 1600 °C, because small size ytterbium ion makes $LaYO_3$ more stable at high temperatures.

The main accent in research has been focused on optimization of pore size evolution to find the best sintering regimes. The idea concerns minimizing the average pore size and maximizing the number of pores at current porosity to get fully dense nanoceramics at moderate temperatures. Using undersintered samples, we applied the BJH method to control the pore size distribution and the number of pores in the porosity range of 10-20% in the samples obtained at various ramp-and-hold regimes of sintering. Open porosity only was found at 20% total porosity was found independently on heating mode. The heating rates higher than 12 °C/min resulted in premature pinching off of channel pores at total porosity 17% and formation of isolated coarse-size pores. The same effect has been revealed at lower heating rates than 0.3 °C/min. The best pore size distribution (narrow and minimal average pore size of 35 nm) was found for multistep sintering regime, which exploited rapid heating to residual porosity of 22%, then switching to three times slower heating rate until asting in porosity 17%, then decreasing heating rate two times until porosity 8.5% followed by isothermal sintering until porosity less than 0.1%. The best transparency achieved for Nd:YAG ceramics was 67%. This figure was supposed to be improved using RCS regime and sintering under controlled oxygen partial pressure conditions. The series of sintering experiments has been continued under controlled oxygen partial pressure. It has been revealed that oxygen influences non-linearly on sintering rate: at low relative density the densification rate increases with oxygen partial pressure decrease and at high relative density faster densification and slower grain growth occurs at lower oxygen partial pressure. For the first stage the highest densification rate corresponds to $pO_2=10^{-1}$ atm. and for the second stage where almost all porosity is closed, the best partial pressure is equal to $pO_2=10^{-12}$ atm corresponding to near full density (99.95%). Thus, to get dense and transparent garnet and perovskite ceramics, it is useful to control densification rate (rate-controlled algorithm) and keep variable oxygen partial pressure. The as prepared both Nd:YAG and $Nd:LaYO_3$ ceramics are of 99.95% dense. The 0.06 neodymia doped garnet samples showed good transparency of 70-72% after RCS combined with two-step sintering and isothermal holds for 2-12 hours at 1700 C (Fig. 2.10).
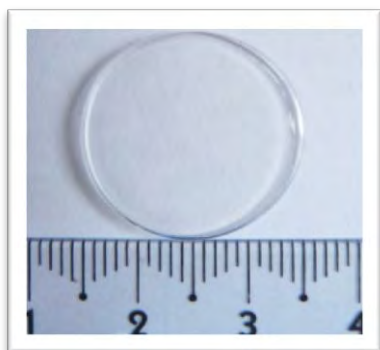
Fig. 2.10 The 006Nd:YAG RCS transparent sample.

The $Yb:LaYO_3$ phase textured under strong magnetic field has demonstrated the best density of the sintered ceramics in the range 99.0-99.9 after the rate controlled sintering. The samples were found semi-transparent (general transparency is less than 45%), but along c-axis perpendicular to tablet plane it is much higher but difficult to be measured (thin tablets). New batch of samples prepared under strong magnetic field is required to measure optical and luminescent properties.

In spite of high relative density achieved for all samples (many samples are denser than 99% of theoretical value), they remain semitransparent and opaque because of several reasons: refraction in non-isotropic solids is variable and grains in non-isotropic ceramics are too big to allow ceramics to be transparent. The semitransparent samples, however, were obtained right after slip casting in magnetic field. We believe, the semi-chaotic/semi-ordered slip casted Nd:LaYO$_3$ samples become semi-transparent. The randomly packed particles and grains after CIP and sintering remained opaque in spite of pore-less state. This means that experimentally we are on the right way to get textured transparent optical material. To achieve higher transparency, the more durable sintering regime (50 and more hours) will be required.

Conclusions

1.   With the aid of X-ray phase analysis, petrography and electron microscopy phase equilibria in ternary ZrO$_2$-CeO$_2$-La$_2$O$_3$, ZrO$_2$-CeO$_2$-Eu$_2$O$_3$, ZrO$_2$-CeO$_2$-Gd$_2$O$_3$ systems and boundary binary ZrO$_2$-Gd$_2$O$_3$, CeO$_2$-La$_2$O$_3$ CeO$_2$-Eu$_2$O$_3$, CeO$_2$-Gd$_2$O$_3$ systems have been studied in the whole interval of concentrations at temperatures 1500-600 °C.

2.   The phase diagram of the ZrO$_2$-Gd$_2$O$_3$ system has been developed. In the ZrO$_2$-Gd$_2$O$_3$ system at 1500 °C there had been found fields of solid solutions based on tetragonal (T) and cubic (F) modifications of ZrO$_2$, monoclinic (B) and cubic (C) modifications of Gd$_2$O$_3$ and ordered phase, which crystallized in the cubic structure of pyrochlore type Gd$_2$Zr$_2$O$_7$ (Py). Lattice parameters were calculated for all phases formed. The state of liquidus of the system has been confirmed from microstructure analysis of the melted/crystallized samples.

3.   The isothermal sections of the ZrO$_2$-CeO$_2$-La$_2$O$_3$ system were studied at 1450, 1250, 1100 °C and of the ZrO$_2$-CeO$_2$-Gd$_2$O$_3$ system at 1450 and 1100 °C.

4.   There has been found that in the ZrO$_2$-CeO$_2$-La$_2$O$_3$ system at 1500-1100 °C the following fields of solid solutions exist: mooclinic (M) and tetragonal (T) ZrO$_2$, hexagonal (A) La$_2$O$_3$, cubic, fluorite-type (F) CeO$_2$ and ordered phase La$_2$Zr$_2$O$_7$ of the pyrochlore type.

5.   In the system ZrO$_2$-CeO$_2$-Gd$_2$O$_3$ at 1450, 1100 °C, the following solid solutions were studied: monoclinic (B and M), tetragonal (T), cubic (C and F) REO and ZrO$_2$, respectively, and the pyrochlore-type intermediate phase Gd$_2$Zr$_2$O$_7$ (Py). It was revealed that in the ZrO$_2$-CeO$_2$-Gd$_2$O$_3$ system the phases of cubic symmetry predominate such as: F − Fm3m, Py – Fd3m, C - Ia3.

6.   First phase reactions in the boundary binary systems CeO$_2$-La$_2$O$_3$ CeO$_2$-Eu$_2$O$_3$, CeO$_2$-Gd$_2$O$_3$ were studied at the following temperatures: 1500, 1100, 600 °C. Lattice parameters were studied versus concentrations and refraction indexes has been established for several solid solutions.

7.   In the system CeO$_2$-La$_2$O$_3$ at 1500-1100 °C two types of solid solutions form: cubic, fluorite-type F-CeO$_2$ and hexagonal A-La$_2$O$_3$, which are divided by two-phase field (A+F)

8.   The solid phase reaction of CeO$_2$ (fluorite, F) and Eu$_2$O$_3$ (monoclinic, B) showed, that in the CeO$_2$-Eu$_2$O$_3$ system at 1500 °C three types of solid solutions are formed: cubic of fluorite type F-CeO$_2$ and C-Eu$_2$O$_3$, as well as monoclinic B-Eu$_2$O$_3$, divided by two-phase fields (F+C) and (C+B). B phase of Gd$_2$O$_3$ was established to exist until 1000 °C.

9.   In the system CeO$_2$-Eu$_2$O$_3$ at temperatures 600-1500 °C in the concenration range from 0 to 15 mol % Eu$_2$O$_3$ the cubic solid solution F-CeO$_2$ formed. For these solid solutions F-CeO$_2$ grain size remains in the nanoscale range from 41 to 81 нм.

10.   First the solid phase reaction between CeO$_2$ and Gd$_2$O$_3$ at temperatures 1500-600 °C the following solid solutions are formed: cubic, fluorite type F-CeO$_2$ and C- Gd$_2$O$_3$, monoclinic B-Gd$_2$O$_3$.

11.   The solubility of Gd$_2$O$_3$ in F- CeO$_2$ achieved ~10 mol % at 1100 °C and 15 mol % at 1500 °C. At 600 °C two types of solid solutions were found: cubic, fluorite-type F-CeO$_2$ and C- Gd$_2$O$_3$, which divided by two-phase field (F+C).

12.   The results can be used for optimization of dopant concentration in the novel composite materials ionic conductors and catalytic systems.

13.   The co-precipitation method was used to prepare nanosize powders of Nd:YAG, Nd:LaYO$_3$ and Yb:LaYO$_3$ solid solutions. The powders have been prepared and characterized. The nanosize powders of doped Nd:LaYO$_3$, Nd:Y$_3$Al$_5$O$_{12}$ and Yb:LaYO$_3$ phases containing various amount of neodymia ranged from 0.06 to 10 at% have been chemically prepared. The particle size distribution has shown mean particle size ranged 10-22 nm assembled to agglomerates of 40-120 nm in size.

14.   The as prepared nanopowders were subjected to slip casting technique in strong magnetic field (12T) for anisotropic ceramics, or tape casting technique without fields for isotropic ceramics, annealed, followed by sintered at 1500-1700 °C for 2-12 hours until near full density. The 0.06 neodymia doped garnet samples showed the best transparency of 70-72% after RCS combined with two-step sintering mode. The best density of the sintered ceramics of 99.5-99.9 was achieved for neodymia-doped YAG. The anisotropic ceramics of Yb:LaYO$_3$ was obtained in near fully dense state, mosly optically semi-transparent or opaque. The best transparency achieved 45%.

15.   Further efforts of anisotropic laser ceramics manufacturing are necessary to increase transparency to 80% or higher. This requires much perfect powder synthesis technique and improved other powder manipulation operations mostly control of orientation on slip casting. Sintering technique also needs perfectness of performance to allow reducing the grain growth in anisotropic ceramics and increasing its transparency.

Plan of publications in 2015.

1 Andrievskaya E.R., Gusarov V.V., Kornienko O.A., Sameljuk A.V., Sayir A., Phase relation studies in the ZrO_2-CeO_2-La_2O_3 system at 1100 °C // Journal of the American Ceramic Society. – May 2015

2 Andrievskaya E.R., Kornienko O.A., Sameljuk A.V., Sayir A. Phase Relation Studies in the CeO_2-Er_2O_3 System at 1100-1500 °C // Journal of the European Ceramic Society. – February 2015

3 Andrievskaya E.R., Kornienko O.A., Sameljuk A.V., Sayir A. Phase Relation Studies in the CeO_2-Eu_2O_3 System at 600-1500 °C // Journal of Materials Science and Engineering A & B, David Publishing Company – February 2015

4 Andrievskaya E.R., Kornienko O.A., Sameljuk A.V., Sayir A. Phase Eqiuilibria in the ternary ZrO_2-CeO_2-Eu_2O_3 System at 1500 °C // Journal of the European Ceramic Society - March 2015

5 Chudinovich O.V., Andrievskaya E.R., Ragulya A.V., Sayir A. Synthesis of Nd:$LaYO_3$ and Yb:$LaYO_3$ nanocrystalline powders. Ceramics International. March 2015

6 Andrievskaya E.R., Chudinovich O.V.,Kovylyaev V.V., Sayir A. Phase relations in the La_2O_3-Y_2O_3 Nd_2O_3 at 1500 °C. Journal of the European Ceramic Society – April 2015

7 Ragulya A.V., Andrievskaya E.R., Chudinovich O.V., Sayir A. Fabrication and spectral properties of Yb^{3+}-doped $LaYO_3$ nanocrystalline transparent ceramics. Optical materials – May 2015

Perspectives of research.

Present results achieved through this project proved prospectiveness of the following works:

The future trends of our research are grounded on understanding the following advantages. Advanced ceramic approaches enable producing of composite laser ceramics with waveguide, laminar-structured, gradient doping for new pumping architectures [A.Ikesue, Y.L.Aung, Ceramic laser materials, Nature Photonics **2** (2008) 721-727.]. This is why some experts predict that in near future most solid-state lasers may be built with ceramic materials [Research Opportunities in High Energy and High Average Power Lasers High Average Power Lasers / Study for the Air Force Office of Scientific Research, 2009.]. Moreover, near pore-free transparent ceramics even with non-cubic structure (anisotropic) can be obtained by ceramic processing as textured materials as new host for solid-state lasers which cannot be grown by traditional melt methods [G.L. Messing, A.J. Stevenson, Toward pore-free ceramics, Science 322 (2008) 383–384. T. Taira, Domain-controlled laser ceramics toward Giant Micro-photonics, OPTICAL MATERIALS EXPRESS 5 (2011) 1040-1050.].

Preliminary experiments were helpful to reveal several challenges of obtaining the textured and transparent ceramics based on anisotropic (non-cubic) phases such as LaYO3: i) synthesis of highly

crystalline and submicron size particles valid for colloidal orientation in strong magnetic field; this search has been finished during the present project, nevertheless the control of stoichiometry for LaYO3 doped with REO is still open because of water sorption by REO ii) search of sintering mode (including controlled oxygen partial pressure) valid to get near fully dense transparent ceramic is in progress. Neodymium oxide was found to worsen stability of the LaYO3 phase. We came to conclusion that rear earth ions with smaller ionic size than Nd3+ must be used as laser dopants, such as Eu3+ and Yb3+.

Complex oxide phases $LnLn'O_3$ (Ln, Ln'=Rare Earth Ions) with perovskite structure possess unique combination of electrical, magnetic and optical properties. They are promising materials as high-K dielectrics materials. The proposed systems have not been studied as potential optical materials.

Study of the phase equilibria in the ternary systems $Ln':LaLnO_3$, where Ln=Ho,Tm,Lu, but Ln'= Eu,Yb,Dy.. The physic-chemical properties of compounds formed in the systems as well as ordering and decomposition temperatures of perovskite-like phases ($LaLnO_3$) doped by Dy^{3+}, Eu^{3+} and Yb^{3+} will be studied. The optimal compositions to produce optical ceramics will be determined and transparent ceramics will be obtained by nonconventional consolidation methods.

1. Study the perovskite-like phase stability depending the temperature and ionic radii of dopant;
2. further manufacturing steps of anisotropic and textured laser ceramics based on $LaLnO_3$ compounds using slip casting in magnetic field followed by special sintering techniques;
3. study of stability the $LaLnO_3$ phases against temperature and laser dopant concentration;
4. Microwave sintering of optical ceramics in the atmosphere with controlled partial pressure of oxygen.

The proposed lasers will significantly improve measurement accuracy of distances as well as implement new modes of laser processing of materials, and to create a qualitatively new optical storage media. Potential consumers of ceramic-based microchip lasers are the companies that are developing laser range finders and radar systems, organizations involved in laser processing of materials, research institutes developing optical processing, information transmission and storage systems.

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Introduction

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1.   E.R. Andrievskaya, O.A. Kornienko, A.V. Sameljuk, Ali Sayir, Yoshio Sakka, Phase equilibria in the system ZrO_2-CeO_2-La_2O_3 // Abstract of paper 4th International Conference Materials and Technologies "SMART MATERIALS, STRUCTURES AND SYSTEMS" CIMTEC 2012. Montecatini Terme, Tuscany, Italy, June 10-14, 2012. *A1:P01*.
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